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TURBINE FUELS FROM TAR SANDS BITUMEN AND HEAVY OIL PART 1/2

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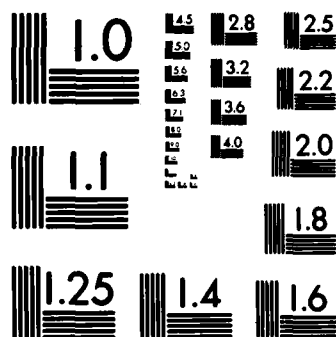
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PART II

TURBINE FUELS FROM TAR SANDS BITUMEN
AND HEAVY OIL

PHASE II - Laboratory Sample Production

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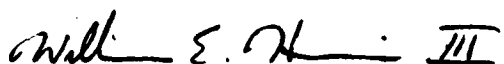
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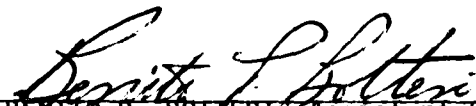


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19. ABSTRACT (Continue on reverse if necessary and identify by block number) The conversion of domestic tar sands bitumens or heavy crude oils into aviation turbine fuels has been studied in small scale equipment to demonstrate the process scheme consisting of hydrovisbreaking the bitumen or crude residuum followed by catalytic hydrotreating or hydrocracking of the resultant naphtha or distillate fractions. Four different feedstocks were employed; two were bitumens (from Kentucky or Utah) and two were heavy crudes from California. Significant operating parameters were examined for each process step. Prototype naphtha and kerosene type fuel samples compared well with JP-4 and JP-8 specifications, although fuels prepared from Utah bitumen (Sunnyside deposit) were deficient in freeze point. Initiation of Phase III, pilot plant scale evaluation of the process, is recommended.						
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SUMMARY

Domestic tar sands bitumen and heavy crude oils represent significant resources, in terms of the volume of fuel consumed annually by the U.S. Department of Defense. To realize this potential, however, these resources must be convertible into high quality aviation turbine fuels. During Phase I of this program, several process routes were identified that could achieve this conversion efficiently and at relatively high yields. Of the assorted process sequences evaluated, one particular two-step operation was recommended for further study. In the first step, raw bitumen or heavy crude residue was processed under hydrovisbreaking conditions, to achieve high conversion of the non-distillable components into distillable liquid. In the second step, the hydrovisbroken intermediate stream, plus any straight run fraction that bypassed the upgrader, was catalytically hydrotreated or hydrocracked to produce aviation turbine fuel components in the requisite distillation range.

Phase II work, which is covered in this report, consisted of bench or laboratory scale experiments with four different low quality feeds to demonstrate the processing scheme. The four feeds included two heavy crudes from California (Hondo Monterey and San Ardo) and tar sands bitumens from Kentucky (Kensyntar) and from Utah (Sunnyside). Feedstock preparation consisted of desalting, demineralization, solvent stripping, and distillation into straight run fractions, tailored to the needs of the individual feeds.

Batch hydrovisbreaking was carried out with each feed in a 10-gallon high pressure autoclave, where time, temperature and pressure effects were determined. Modest feedstock effects could also be extracted from the experimental data. Generally, however, whether a bitumen or an atmospheric crude residue was being processed, product distributions were similar when compared at constant conversion of the $>1,000^{\circ}\text{F}$ fraction of the charge. For a 2-hour reaction time at 2,500 psig, 80 volume percent conversion could be achieved with temperatures in the range of 750 to 800°F.

The hydrovisbroken liquid products were composited according to feedstock, and distilled into naphtha (initial to 490°F) and distillate (490 to 1,000°F) fractions for further processing. In the case of the two heavy crudes, the straight run naphtha and middle distillate fractions removed from the crude initially were combined with the respective hydrovisbroken fractions before hydrotreating.

The four different naphthas were hydroprocessed in a small, fixed bed, continuous flow reactor over a non-proprietary nickel-molybdenum on alumina catalyst. Product sulfur and nitrogen contents of less than 1 ppmw were readily achieved at 1,250 psig, 675°F, and 1.25 hr⁻¹ space velocity. There were indications that even less severe processing conditions would also have been acceptable; however, the experimental design utilized did not effectively determine the processing requirements unique to each feed.

The four different distillates were hydrocracked in a non-integrated two-reactor configuration. In the first reactor, feeds were hydroprocessed over the same catalyst as was used in the naphtha hydrotreating studies. The objective was to reduce total nitrogen content, which ranged from 3,400 to >8,000 ppmw in the feeds, to a range of 10-20 ppmw in the products. This was accomplished for each feed, with the highest nitrogen content San Ardo distillate requiring somewhat more severe processing conditions than the other three feeds -- 0.5 hr⁻¹ space velocity at 750°F and 2,500 psig vs. 0.7 hr⁻¹ space velocity at 750°F and 2,000 psig.

Hydrotreated distillates were once-through hydrocracked over a nickel-molybdenum on crystalline silica-alumina catalyst. When processed at 610°F and 2,000 psig, there was some differentiation among the four feeds evident, as estimated by the space velocity required to produce a given conversion level. The Kensyntar feed required a 2.2 hr⁻¹ space velocity, while the Sunnyside and San Ardo feeds could be processed at 3.7 hr⁻¹. At constant conversion, however, product distributions for the four feeds were very similar.

Both naphtha type and kerosene type aviation turbine fuels were prepared from the hydrotreated and hydrocracked products representing each feed. Comparisons with specification requirements for JP-4 and JP-8 fuels were generally good. However, both fuels prepared from the Sunnyside bitumen were deficient in freeze point by 10 degrees Fahrenheit. This is not considered to be a major obstacle at this time, since it is expected that the freeze points would respond to changes in processing or distillation conditions. There were no attempts to improve the Sunnyside-derived fuel freeze points in this program.

It was recommended that Phase III of the program be initiated. In Phase III, larger scale pilot plant operations would be carried out to provide data for developing an engineering plant design and cost estimate as well as to provide larger volumes of prototype fuels for more comprehensive testing.

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FOREWORD

This report presents the results of a study performed by the Applied Research and Development (ARD) Department of the Sun Refining and Marketing Company, a subsidiary of Sun Company. The program was supported by the Aero Propulsion Laboratory of the U.S. Air Force Wright Aeronautical Laboratories under Contract No. F33615-83-C-2352, awarded 8 July 1983. It addresses the technology of converting tar sands bitumens and heavy petroleum crude oils into aviation turbine fuels for military use.

The work was performed at the Sun Company ARD laboratories in Marcus Hook, Pennsylvania during the period 1 October 1983 through 31 October 1985. The Air Force Project Engineer during this period was Captain William E. Harrison, III AFWAL/POSF. The ARD Program Manager was Mr. Alfred F. Talbot. This report was released by the author in January, 1986.

The Program Manager acknowledges the valued contributions of co-workers V. Elanchenny, J. P. Schwedock, and J. R. Swesey in the execution of this program. ARD management's provision of vital resources during a prolonged strike of hourly workers at Sun Co.'s Marcus Hook facility in mid-1984 enabled progress to be maintained during an especially difficult period. The dedicated efforts of C. J. Bennett in preparing the manuscript are also acknowledged and greatly appreciated.

The Program Manager also expresses appreciation to Captain William E. Harrison for his continued support and guidance in meeting the assorted administrative, logistical, and technical challenges attending the project.

This interim report describes the results of the second phase of a planned three-phase assessment of the potential for producing military aviation turbine fuels from domestic deposits of tar sands bitumens and heavy crude oils. Phase I consisted of a preliminary screening of several combinations of upgrading and refining processes, based on published descriptions or in-house familiarity with these processes. The processing route recommended for further evaluation, as a result of these Phase I studies, consisted of upgrading by hydrovisbreaking, followed by hydrotreating of the lower boiling liquid fractions and catalytic hydrocracking of the higher boiling liquid fractions, to produce specification quality JP-4 or JP-8.

In Phase II, laboratory or bench scale experiments were carried out: 1) to demonstrate the selected process sequence with a selection of low grade feeds, 2) to identify the critical operating parameters, and 3) to prepare experimental quantities of prototype turbine fuel samples for further evaluation.

In Phase III, the recommended process sequence will be carried out with a single feedstock in pilot plant scale equipment in order: 1) to provide operating results to support a preliminary plant design and estimates of fuel manufacturing cost, 2) to identify areas of opportunity for further process improvements, and 3) to provide larger volume fuel samples for more detailed testing.

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GLOSSARY OF TERMS

API Gravity	an arbitrary specific gravity scale, applied to petroleum crudes and products, defined as: $^{\circ}\text{API} = (141.5/\text{specific gravity } 60^{\circ}\text{F}) - 131.5$
barrel	for petroleum usage, 42 U.S. liquid gallons.
bitumen	a naturally-occurring hydrocarbon which is too viscous to flow at the reservoir conditions.
centipoise	a measure of the dynamic viscosity, or resistive flow, of a fluid. One poise (P) equals one dyne-second per centimeter squared.
distillate	a distillable petroleum fraction with a boiling range higher than that of naphtha and excluding vacuum residue. The term middle distillate implies an atmospheric fraction, containing no vacuum distillate.
factorial design	a set of experiments in which pre-selected levels of independent variables are maintained while system response is being determined. In a 2^2 design, two variables are examined at each of two levels; in a 2^3 design, three variables are examined at two levels each.
fuel oil equivalent	used to define quantity of fuel gas in terms of heating value of fuel oil, which is 6.05 million BTU's per barrel.
heavy crude oil	crude oil which has a specific gravity less than 20°F API and is mobile at reservoir conditions.
heteroatoms	used to denote atoms other than carbon and hydrogen contained in organic compounds or structures; applied principally to sulfur, nitrogen and oxygen atoms.
hydrodenitrogenation	reduction in the amount of nitrogen in a feedstock by processing in a hydrogen-containing atmosphere, usually with aid of a catalyst.
hydrodesulfurization	hydrogenative processing of a material to reduce its sulfur content.
hydrovisbreaking	reduction in viscosity of a feedstock under the action of heat and hydrogen.

GLOSSARY OF TERMS (continued)

in-situ	in place; in this context, within the crude oil reservoir or tar sand deposit.
JP-4	wide cut, gasoline type aviation turbine fuel defined by specification MIL-T-5624L.
JP-8	kerosene type aviation turbine fuel defined by specification MIL-T-83133A.
naphtha	a distillable petroleum fraction the boiling range of which falls between those of pentane and gas oil.
refining	in this study, refers to the secondary processing steps which follow upgrading, to produce marketable products from refinery intermediates.
reserves	the amount of fossil hydrocarbon contained within a deposit that is calculated or estimated to be recoverable.
residue	synonymous with resid, residua, residuum; the higher boiling portion of a crude or intermediate which is not distillable without degradation; a long resid refers to tower bottoms from distillation at atmospheric pressure; a short resid to bottoms from vacuum distillation.
resource	the total amount of fossil hydrocarbon contained within a deposit, without regard to recoverability.
simulated distillation	a determination of the boiling range distribution of a hydrocarbon product by application of gas chromatographic methodology; formalized as ASTM Method D2887.
space velocity	an expression of reaction severity, referring to volume of reactant(s) per volume of reactor volume per unit time; usual units are reciprocal hours (hr^{-1}).
specific gravity	mass per unit volume of a material, compared to that of a reference material (often water) at standard conditions (e.g. 60°F).
straight run	refers to a distillate fraction obtained from a crude oil not previously exposed to conditions which would produce appreciable change in chemical structure.

GLOSSARY OF TERMS (concluded)

synthetic crude	a wide boiling range product stream that has been subjected to conditions which brought about an appreciable change in the original chemical structure, in one or a combination of processing steps; also referred to as "syncrude".
tar sands	deposits of mineral, whether consolidated (rock-like) or unconsolidated (sand-like), which have intimately associated with them a significant amount of bitumen.
tower bottoms	the bottom fraction produced from a distillation column; depending on its boiling range, it may or may not be non-distillable, i.e., a residuum.
upgrading	in this study, refers to the primary conversion step in a sequence of processing steps for converting very low quality feedstocks to marketable products; generally excludes those operations which do not result in an appreciable change in chemical structure, such as fractionation, desalting.

LIST OF SYMBOLS AND ABBREVIATIONS

Symbols

0	at
°API	degrees API
°F	degrees Fahrenheit
>650°F	exceeds 650°F (as in a fraction boiling above 650°F)
<500°F	less than 500°F (as in a fraction boiling below 500°F)
>>	very much greater than
<	less than
C ₃	hydrocarbons containing three carbon atoms
C ₄	hydrocarbons containing four carbon atoms
C ₅	hydrocarbons containing five carbon atoms
C ₆	hydrocarbons containing six carbon atoms
H ₂	hydrogen
H ₂ S	hydrogen sulfide
H/C	hydrogen to carbon ratio
%	percent
#	pounds
R-1	reactor number one
R-2	reactor number two
hr ⁻¹	reciprocal hours (i.e. 1/hours)
v/hr/v	volumes per hour per volume, as in space velocity
-	approximately

Abbreviations

API	American Petroleum Institute
ARD	Sun Co.'s Applied Research and Development Department
ASTM	American Society of Testing and Materials
bbl	barrel
BPD	barrels per day

LIST OF SYMBOLS AND ABBREVIATIONS (concluded)

BPSD	barrels per stream day
BTU	British thermal unit
cSt	centistokes
DOD	Department of Defense
EP	end point
F	Fahrenheit
FBP	final boiling point
FOE	fuel oil equivalent
gal.	gallons
gr	gram
IBP	initial boiling point
init.	initial (as in initial boiling point)
mg	milligrams
ml	milliliter
MM	millions
ppm	parts per million
ppmw	parts per million by weight
lb.	pounds
psig	pounds per square inch gauge
RVP	Reid vapor pressure
sp. gr.	specific gravity
SCF	standard cubic feet
SCF/bbl	standard cubic feet per barrel
M	thousand
vol.	volume
wt.	weight

SECTION I

INTRODUCTION

As both the discovery rate and the production rate of domestic, conventional petroleum crudes continue their declines, the United States must place increasing reliance on imported crude to satisfy its expanding energy needs. Accompanying this growing dependence on foreign crude is a greater vulnerability to supply interruptions caused by socio-political events in the less stable world areas. In response to this potential threat, an assessment of process schemes to convert domestically produced low grade feedstocks into high quality aviation turbine fuels was initiated by the Air Force Wright Aeronautical Laboratories.

A demonstration of the suitability of current or new process technologies in this application is critical, inasmuch as the bulk of the petroleum refining capability installed in this country is directed toward the conversion of conventional feedstocks into transportation fuels principally in the gasoline boiling range. Application of conventional refining technology to low grade feedstocks produces either low yields of the critical middle distillate boiling range material or, if yield patterns are shifted to compensate for the inadequate straight run content, material of decidedly lower quality. As current Canadian experience illustrates, distillate fuel combustion quality can suffer as the proportion of synthetic crude produced from tar sands bitumen increases. Accordingly, information about the quality of the fuels produced, as well as their cost, is an essential element of this investigation.

Overall program objectives comprising this assessment include the following:

- to identify a preferred processing scheme for producing JP-4 or JP-8 from bitumens/heavy crudes.

- to demonstrate its performance by supplying fuel samples at both laboratory and pilot plant scale.
- to perform an economic analysis of the fuel manufacturing venture, based on the preferred processing scheme.
- to determine the sensitivity of fuel selling price to variations in fuel quality produced by varying processing severity.

The program has been structured into three discrete phases, consisting of the following:

Phase I - Preliminary process analysis includes an evaluation of the potential of domestic tar sands and heavy oil resources to help satisfy the nation's requirements for military transportation fuels; screening of candidates, and selection for further investigation, of a preferred processing route for conversion of these low quality feedstocks into high quality, finished fuel products; and preliminary estimates of fuel manufacturing costs based on the selected processing schemes. The sensitivity of the processing scheme(s) to design parameters such as feedstock source, projected product slate, and plant capacity is also to be examined.

Phase II - Laboratory sample production includes investigation and definition of the principal operating variables for the major processing steps comprising the recommended process scheme identified in the Phase I studies; small samples of prototype fuel made according to the recommended processing scheme are to be prepared for evaluation by the Air Force; adjustments, as necessary, to the Phase I preliminary estimates of fuel costs will be made to reflect results of the laboratory tests.

Phase III - Pilot plant testing, final design and economics includes confirmation of the laboratory-estimated process operating parameters in continuous type pilot plant studies; development of design bases for detailed commercial plant cost estimates; economic analysis of fuel costs, including sensitivity to various economic assumptions; estimates of cost/quality/processing tradeoffs for production of fuels of varying quality; and preparation of pilot-plant sized samples of both specification and variable quality fuels.

Opportunities to review progress through each Phase of the program, and to decide on whether to proceed to the next succeeding program segment, are afforded by comprehensive contractor presentations.

The results of the Phase I effort by Sun Co.'s Applied Research and Development (ARD) Department have been reported separately (Reference 1). In brief, those findings were:

- though small compared to some world-wide deposits, domestic bitumen and heavy crude oil resources represent a significant production potential when compared to the peace-time fuel needs of the U.S. Department of Defense.
- conversion of these low quality reserves into specification quality aviation turbine fuels poses a significant processing challenge.
- a two-step approach to the processing problem was formulated, viz. 1) upgrade the low quality feedstock into an intermediate stream which more closely resembles a conventional petroleum crude oil, and 2) refine various portions of the intermediate stream into finished fuel or fuel blending components.
- case studies were formulated for comparison, based on published information, vendor contacts, and in-house experience. Among the upgrading technologies considered were two carbon rejection type

processes: 1) delayed coking and 2) the proprietary Asphalt Residuum Treating (ART) process and two hydrogen addition type processes: 3) hydrovisbreaking and 4) fixed bed catalytic hydrocracking. Refining processes employed to achieve high yields of aviation turbine fuels were naphtha hydrotreating and distillate hydrocracking. Of the four upgrading processes compared, high conversion hydrovisbreaking appeared the most suitable, based on projected fuel yields, by-product quantities, and fuel manufacturing costs.

It was therefore recommended that the investigation be continued into Phase II, the small scale experimental portion of the program, employing the hydrovisbreaking concept for upgrading the heavy feeds. Figure 1 illustrates the generalized process concept to be demonstrated.

This report presents the results of ARD activities in the Phase II segment of the program, which consisted of the following major elements:

PHASE II LABORATORY SAMPLE PRODUCTION

<u>Task</u>	<u>Activity</u>
1	Feedstock Preparation and Characterization
2	Catalyst Screening
3	Hydrovisbreaking
4	Process Scouting
5	Sample Preparation
6	Process Analysis
7	Phase III Plan
8	Phase II Report

Results of these activities are summarized in the report sections which follow.

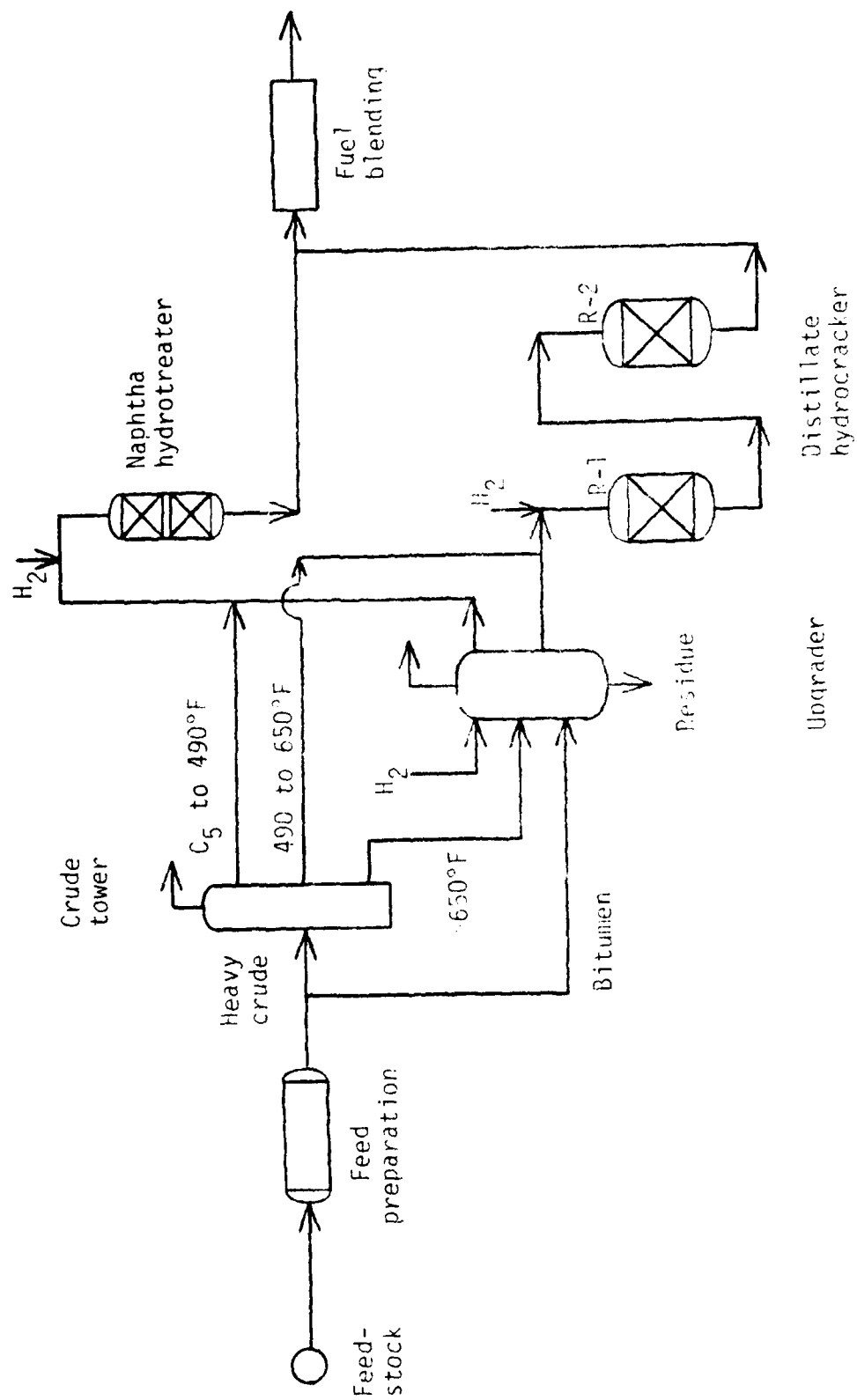


FIGURE 1 PROCESS CONCEPT

SECTION II

FEEDSTOCK PREPARATION AND CHARACTERIZATION

1. Feedstock Acquisition

A brief assessment of the bitumen and heavy oil resources of the United States was performed early in the Phase I segment of this program. An intended output of that study was a recommendation of feedstocks to be included in the Phase II effort. At the time, surveys disclosed as many as 62 domestic pilot or commercial tar sands projects (Reference 2). This was encouraging, since it was planned that the Phase II feedstock selection be weighted toward bitumen, viz., three bitumens and one heavy oil.

Although plans call for only one of the four feeds selected for Phase II evaluation to be examined in the larger scale Phase III work, it was not practical to select that one feed so early in the program. Thus, each of the four feeds was required in sufficient volume --about 1,500 gallons-- to support both the Phase II and Phase III studies. If a second contractor were to evaluate the same feed, the required volumes doubled to 3,000 gallons.

Preliminary contacts with tar sands project operator/sponsor organizations were disappointing. A recent turnaround in the petroleum supply/demand situation resulted in diminished interest in commercialization, in shut-down of some projects, and in postponement of others. Few had both the interest and capability to supply the desired quantities. Thus, the selection of feedstocks for Phase II work resulted less from a consideration of the technical and economic factors emerging from the Phase I estimate than it did from simply a supply capability standpoint.

A somewhat different supply dilemma was encountered when considering the heavy crude oil feedstock candidate. Sun Company currently had no appropriate captive production, i.e., low API gravity, high sulfur content,

high reserve potential. Recent offshore discoveries looked promising but the fields were not producing, nor were the crudes very thoroughly characterized. A volume problem of another sort arose in dealings with operators who were already producing heavy crudes on the West Coast. Whereas the 1,500 to 3,000 gallon requirement for bitumen was too large for many tar sands projects, it was too small for efficient handling by many heavy crude production or refining organizations. For them, drumming off 3,000 gallons was impractical with the labor force available.

Numerous inquiries by both Air Force and ARD representatives finally identified four suppliers for the Phase II feedstocks. Once all details regarding the four shipments were worked out, procurement contracts were placed by the Defense Fuel Supply Center, Cameron Station, Virginia. Only two bitumens could be secured, and only one of those in sufficient volume to support a possible Phase III effort, if needed. The other two feeds were heavy crude oils, both from California. In one instance, the crude was only available in bulk, which required that a tank wagon load be obtained. The full tanker load was delivered to the ARD laboratories, unloaded into drums, and half the drums shipped to a second contractor, Ashland Oil.

The four feedstocks obtained for the Phase II program were:

- approximately 1,500 gallons of a heavy crude oil produced from the Hondo Monterey field in the Santa Barbara Channel of offshore California.
- approximately 1,500 gallons of a heavy crude oil produced from the onshore San Ardo field in the coastal regions of southern Monterey County in California.
- approximately 1,500 gallons bitumen received from Kensyntar Company, produced from the Big Clifty formation in Edmonson County, Kentucky by in-situ wet combustion technique.

- approximately 440 gallons of a blend of about 20-weight-percent bitumen in a kerosene carrier, from Colorado School of Mines Research Institute. The bitumen was from the Sunnyside, Utah deposit and had been extracted and concentrated by solvent-assisted water flotation.

2. Feedstock Preparation

Preliminary inspection of the as-received feedstocks indicated some pretreatment was required before the process studies could be started. The extent of pretreatment varied, and was specific to the individual feedstock. Nominal operating conditions for the various pretreatment operations are indicated in Table 1, and included:

- Hondo Monterey (California) crude was desalted in a batch mode. The desalted whole crude was then distilled into naphtha (initial to 490°F), middle distillate (490° to 650°F) and atmospheric residue (>650°F) cuts in continuous mode pilot plant distillation equipment. The straight run overhead fractions were retained for subsequent blending with hydrovisbroken naphtha and distillate fractions. The atmospheric residue was retained for processing at hydrovisbreaking conditions.
- San Ardo (California) crude was also batch desalted, but with added solvent (toluene) to reduce its high viscosity at the desalting temperature. The desalted solvent/crude blend was first stripped of solvent, then distilled into naphtha (initial to 490°), middle distillate (490° to 650°F), and atmospheric residue (>650°F) cuts. The straight run naphtha and middle distillate fractions were retained for blending with the respective hydrovisbroken fractions, while the atmospheric residue was also held for subsequent processing at hydrovisbreaking conditions.

TABLE 1

FEEDSTOCK PREPARATION

Feed Type	Objectives	Pretreatment Conditions (1)	Quantity treated, gal.	Results (2)		Distillation (3)	
				Before	After	Fraction	Yield, vol%
				a	b	a	b
Heavy crude							
Hondo	Desalt, fractionate	180°F, 40ppm additive, two 50% water washes	200	28	150	1	0.6
Monterey						Init.-490°F	15
						490-650°F	10
						>650°F	75
San Ardo	Desalt, fractionate	180°F, 25% toluene, 40ppm additive, two 50% water washes	200	-	32	1	-
						Init.-490°F	10
						490-650°F	10
						>650°F	80
Bitumen							
Kensyntar bitumen	Desalt	180°F, 25% toluene, 40ppm additive, two 50% water washes	200	400	37	0.7	48
							(Solvent recovery, only)
Sunny-side bitumen	Demineralize, strip diluent	180°F, 50ppm additive, one 20% water wash	400	0.85	0.0	0.0	0.0
							(Diluent removal, only)

(1) For desalting or demineralizing, only. Performed in agitated, glass-lined, jacketed, 500-gallon kettle.

(2) For desalting operations, values represent lb salt per 1000 bbls as determined by a) conductivity method ASTM D3230 or b) colorimetric titration of chloride ion in water extract of crude. For demineralizing operation, figures represent wt% solids via modified Soxhlet extraction

(3) Distillation conditions varied with type of still and application

- Kensitytar (Kentucky) bitumen was also desalted in batch mode facilities. It, too, required toluene solvent to reduce its viscosity at desalting conditions. The desalted blend was stripped of solvent, and the recovered full-boiling bitumen subsequently processed at hydrovisbreaking conditions.
- Sunnyside (Utah) bitumen was received as a ca. 20% solution in kerosene (boiling point ~425°F). In addition, it contained a significant amount of solids, some water, and appeared to be of variable quality across the eight-drum shipment. A significant laboratory program was carried out to develop a method for quantifying water and mineral content and for removal of these contaminants from the as-received material. Neither centrifugation nor filtration were effective, whereas a procedure based on additive-assisted gravity settling did prove effective in rejecting much of the mineral matter. After demineralizing, the kerosene/bitumen blend was fractionated to remove water and kerosene. The still bottoms were subsequently processed at hydrovisbreaking conditions.

The effectiveness of the desalting and/or demineralizing operations are also indicated in Table 1. Two different methods of determining salt content were applied. The occasionally poor correspondence between the two techniques is not uncommon when dealing with very heavy crudes. As shown in Table 1, however, the pretreatment methods employed were effective in reducing the contaminants to more acceptable levels.

3. Feedstock Properties

Physical and chemical characteristics of three of the heavy feeds were determined on an as-received basis. The fourth feed (Sunnyside bitumen) was received as a dilute solution in kerosene and was contaminated with solids. As indicated in the preceding section, the minerals content was reduced, and most of the kerosene was removed as a result of extensive pretreatment. However, high variability in some of the test data suggests the bitumen fraction recovered was not of uniform composition. Thus, the data reported for the Sunnyside bitumen should be viewed with reservation.

Table 2 lists physical and chemical characteristics of the four feeds. The lightest in terms of API gravity was the Hondo Monterey crude, which contained a modest volume of material in the gasoline boiling range. The gasoline content of the other three feeds ranged from slight to nil. Other physical properties such as flash point, pour point and viscosities were generally consistent with these variations in boiling range.

The carbon-to-hydrogen ratio of the Hondo crude was significantly less than for the other three feeds, a reflection of the higher proportion of light boiling distillates. Sulfur contents ranged from a low of 0.32 weight percent for the Sunnyside bitumen to above 4 weight percent for the Hondo. All four feeds had relatively high nitrogen contents, but the San Ardo feed was especially noteworthy with 1.2 weight percent nitrogen. Ash content of both bitumens was high, at greater than 1 weight percent. The value of nearly 2 weight percent for the Sunnyside bitumen suggests the demineralization pretreatment was not completely effective. Among the trace metals measured, nickel and vanadium are considered naturally occurring. Though higher than are found in many clean, light petroleum crude oils, the values were well below levels reported for some heavy crude oils produced from the Caribbean basin and were not expected to be major obstacles during processing.

The feedstocks listed in Table 2 were fractionated into several overhead cuts and a residue fraction by a true boiling point distillation, to help determine the appropriate processing scheme for each feed. A limited number of physical and chemical properties was determined on each cut. These data are included as Appendix A, Tables A-1 through A-4. As a result of this evaluation, it was decided that the two heavy crude oils would have the naphtha and atmospheric gas oils fractions removed and only the atmospheric residue (i.e. the >650°F fraction) processed at hydrovisbreaking conditions. On the other hand, the two bitumens would be charged to hydrovisbreaking as the full boiling range materials, as recovered from the desalting/solvent stripping operation.

TABLE 2

PROPERTIES OF PHASE II FEEDSTOCKS

Type Source	Heavy crude oil		Bitumen	
	<u>Hondo</u> <u>Monterey</u>	<u>San Ardo</u>	<u>Kensyntar</u>	<u>Sunnyside</u> (2)
<u>Physical properties</u> (1)				
Gravity, °API	18.7	12.8	9.8	11.9
Sp. gravity, 60/60°F	0.9421	0.9806	1.0014	0.9868
Distillation, °F 0 ____ % (by ASTM D1160)				
IBP	155	183	508	214
5	174	401	590	449
10	194	494	630	505
20	450	589	713	587
30	601	675	801	782
40	749	769	898	877
50	828	880	-	906
60	-	968	-	-
Flash point, °F	<70	194	350	215
Pour point, °F	-10	35	65	90, >120
Salt, lb/1000 bbl.	28	34	400	0.7
Carbon residue, %	8.5	8.7	9.5	13.2, 17.0
Viscosity, cSt 0 ____ °F				
77	504.9	12,700	-	-
100	223.7	3,294	-	-
160	-	-	839.1	4,862
210	-	-	108.0	674
<u>Chemical analysis, by weight</u>				
Carbon, %	81.00	81.62	85.45	84.04
Hydrogen, %	11.23	10.51	10.56	10.78
Oxygen, %	1.84	1.82	1.18	1.02
Sulfur, %	4.38	1.89	1.49	0.32
Nitrogen, total, %	0.86	1.32	0.40	0.79
basic, %	0.14	0.23	0.21	0.64
Ash, %	0.07	0.12	1.16	1.9
Trace metals, ppm				
Nickel	25,23	41,78	60,50	11,29
Vanadium	165,100	37,96	143,125	135,13
Iron	6,2.3	37,42	813,735	304,1600
Copper	0.4,0.4	0.3,0.9	3,-	0.7,19.0
Hydrocarbon type, %				
Saturates	18.6	24.0	25.7	22.8
Aromatics	41.0	32.7	32.2	25.4
Polar compounds	22.1	27.2	17.6	27.1
Asphaltenes	18.3	16.1	24.5	24.7

(1) Two values shown for repeat testing.

(2) After treatment to remove solids and diluent

SECTION III

CATALYST SCREENING

1. Introduction

The process scheme for converting heavy crude or bitumen into aviation turbine fuels includes several catalytic processes in the downstream section of the refinery. As shown in Figure 1, the naphtha fraction undergoes catalytic hydrotreatment to provide a stable turbine fuel blending component. An additional volume of turbine fuel blend stock is produced by catalytic hydrocracking of the middle distillate fraction. To maintain activity of the hydrocracking catalyst in R-2, the feed to the hydrocracker is stripped of potential catalyst poisons by catalytic hydrotreatment in R-1. This investigation provided a basis for selecting the catalysts to be used in subsequent bench-scale, continuous mode evaluations of each process step.

Project timing and budget constraints limited the scope of this study. As a result, a number of issues can be raised which could affect the applicability of the results, but which would require considerably more resources to resolve. These include the following:

- four low quality feedstocks of widely different composition are included in the Phase II plan. Each feed probably has unique processing and catalyst requirements for best results. Nevertheless, all four feeds within each class (i.e., naphtha, distillate) were to be processed over the same catalyst composition.
- screening of catalyst activity was to be in a batch reactor immediately following catalyst pre-treatment and several brief break-in runs. Therefore, activity comparisons would be for relatively fresh catalyst, and indicate nothing about long-term performance.

- the catalyst screening studies were begun before feedstock preparation work was completed, so the actual Phase II feeds could not be used. Therefore, surrogate feedstocks derived from commercial delayed coking of Athabasca bitumen at Sun Co.'s tar sands plant in Alberta Province were used for the catalyst screening work.
- two different boiling range fractions required hydrotreating. It was assumed that whichever catalyst was found most suitable in the more demanding distillate hydrotreating application would also be acceptable for the less severe naphtha hydrotreating job. Identification of the best catalyst for the naphtha hydrotreating work would have required different experimental facilities and was not attempted.
- with one exception, catalyst candidates were non-proprietary versions offered commercially by catalyst suppliers. Comparison of their performance with that of those available under license was considered beyond the scope of this study.
- the designation of two process streams for hydrorefining evolved from the target product slate which emphasized JP-4 production. It is not known if processing a 120° to 490°F naphtha and a 490° to 1,000°F distillate is the most efficient scheme, based on overall refinery operations. Hydrotreating other combinations, such as light naphtha plus kerosene plus heavy gas oil, might offer advantages but were not explored.

2. Methodology

Catalyst screening was done in a laboratory-scale stirred reactor. The one-liter stainless steel reactor contained a peripheral catalyst basket, to which was charged 60 ml. catalyst for each series of activity determinations. Reactor heating was by thermostat-controlled heating mantle; cooling, when required, was by internal coil. A bottom drain allowed withdrawal of small (ca. 2 ml.) liquid samples at intervals during the run, as well as removal of liquid product at the end of the run.

Hydrogen was charged to the reactor from a calibrated supply tank to maintain the desired reaction pressure throughout the experiment. The same apparatus was used for both hydrotreating and hydrocracking studies.

All catalysts were supported metal oxides. Presulfiding of the catalysts was performed in-place prior to any trial runs, to convert the metals to the active sulfide form. This was done by processing very clean kerosene, to which had been added enough carbon disulfide to provide approximately a 100% excess of the stoichiometric amount of sulfur required to convert the metal oxides to sulfides. Catalyst sulfidation was achieved by contacting with the spiked kerosene at 600°F and 1,000 psig hydrogen pressure for 2 hours, cooling, and discharging the reactor contents.

Following sulfidation, at least three break-in runs were performed to reduce the initial high activity of the catalyst. The liquid charge for the break-in runs was the same as was used for the experimental studies which followed. The break-in runs were made at 2,000 psig pressure and at a low enough temperature (650°F) that coke deposition on the very active catalyst would be minimal. Sulfur and nitrogen contents of the liquid products from the hydrotreating break-in runs were monitored to confirm that three runs were sufficient to take the initial edge off the catalyst.

At the start of each data run, the reactor was purged with hydrogen and any residual liquid from the preceding run drained from the reactor. Fresh liquid was charged to the reactor via the feed tank, to provide a 6:1 volumetric ratio of oil-to-catalyst at the start of the experiment. With initial hydrogen pressure at 250 psig, the reactor was rapidly heated to run temperature, with stirring. When the reactor contents reached run temperature, the reactor was immediately pressured with additional hydrogen to run pressure, the timer started, and a small liquid sample removed.

During hydrotreating runs, small liquid samples were removed at intervals in the course of a 6-hour period so reaction rate data could be developed. For the 4-hour hydrocracking reaction, only end-of-run samples were evaluated. At the end of the reaction period, the reactor and

contents were quickly cooled to <100°F. The reactor head space was depressured into a gas collection bag, the contents of which were then expelled through a gas meter or into a gas sample bulb for subsequent analysis. Liquid was drained from the reactor and analyzed.

3. Hydrotreating Results

All three catalysts tested were commercially available, supported nickel-molybdenum on alumina compositions, with the following nominal characteristics:

<u>Supplier Code</u>	<u>A</u>	<u>B</u>	<u>C</u>
<u>Composition, wt.%</u>			
NiO	4.0	6.7	4.1
MoO ₃	19.5	27.0	19.8
<u>Support</u>	Alumina	Alumina	Alumina
<u>Form</u>	~1/16-inch shaped extrudate	~1/16-inch cylindrical extrudate	~1/16-inch shaped extrudate

The feed was a raw coker gas oil derived from delayed coking of Athabasca bitumen. Properties of the feed were:

Gravity, °API	16.5
Distillation range by ASTM D1160	
°F @ ___vol%	
5	504
50	710
95	880
Aromatics, wt.%	65
Nitrogen content, ppmw	2,700
Sulfur content, wt.%	3.57

Typical variations in the nitrogen and sulfur contents of the liquid samples with reaction time are illustrated in Figure 2 for a 2,000 psig run. The data show a regular decrease in concentration of each heteroatom with reaction time.

Reaction rates increased with increasing temperature, for all three catalysts. Experimental data were fit to a first order rate expression to generate reaction rate constants for the hydrodenitrogenation reaction. Trends in these rate constants with temperature at 2,000 psig are illustrated by Arrhenius type plots in Figure 3. Although some non-linearity is evident at higher temperatures, rate constants were consistently higher for Catalyst A throughout the range studied.

The reaction was also investigated at 1,500 psig. Trends similar to those reported above for 2,000 psig were observed. While the rate constants for nitrogen removal were lower, the relative ranking of catalyst activities was unchanged. However, analyses of the reaction products indicated that nitrogen content could not be reduced to the desired level (i.e., ~200 ppmw) within the time scale of the experiments.

On the basis of these results, Catalyst A was selected for evaluation in the bench-scale, continuous mode studies to be carried out later.

4. Hydrocracking Results

Three catalysts were also tested for initial activity in the hydrocracking of a wide boiling gas oil. Two commercially available catalyst compositions were supported nickel-tungsten on amorphous silica-alumina. In-house experience with this formulation suggested it might be significantly less active than some of the more recent developments available under process license. Accordingly, the third catalyst of the group was an experimental preparation intended to approximate the performance of these more up-to-date compositions. The experimental material was a supported nickel-molybdenum on crystalline silica-alumina. Nominal characteristics of the three candidates were:

Conditions: 60cc Catalyst A
360cc Coker gas oil feed
725°F
2,000 psig

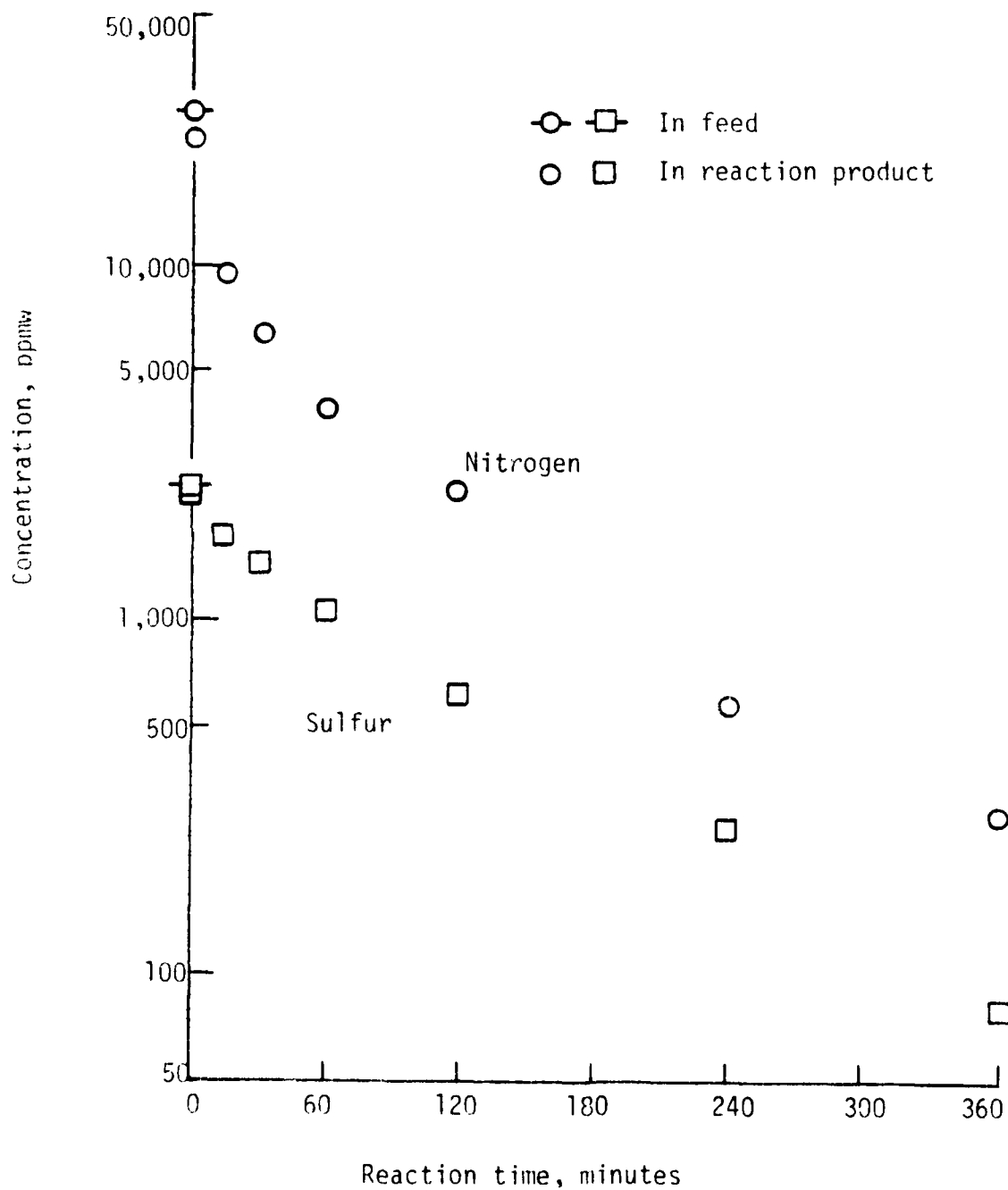


FIGURE 2 TYPICAL BATCH HYDROTREATING RESULTS

Conditions: Batch reactor
60cc catalyst
360cc coker gas oil feed
2,000 psig

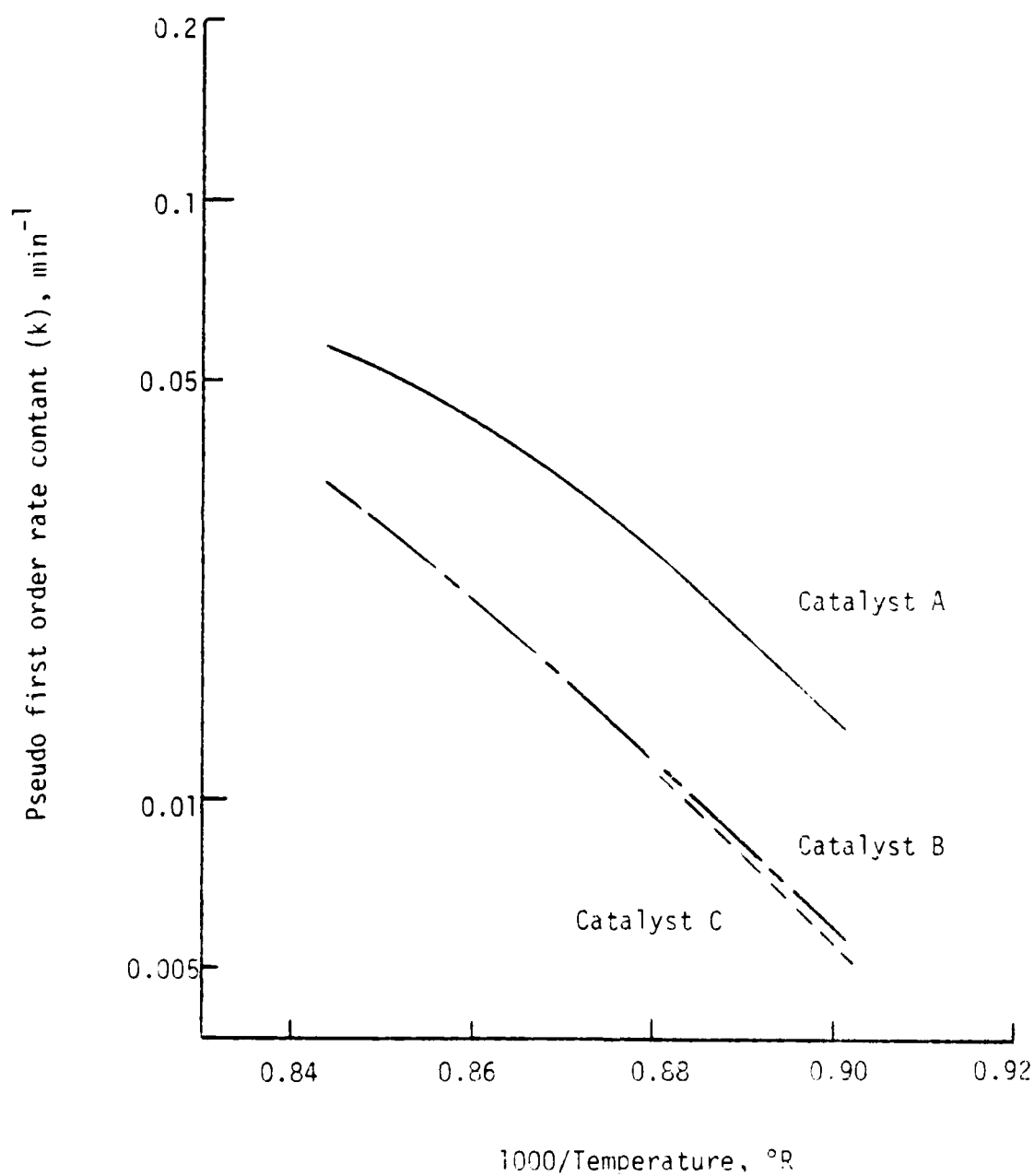


FIGURE 3 COMPARISON OF CATALYST ACTIVITIES
FOR HYDRODENITROGENATION REACTION

<u>Catalyst Code</u>	<u>A</u>	<u>B</u>	<u>C</u>
<u>Composition, wt.%</u>			
NiO	6.5	6.0	7.0
WO ₃	21.0	19.0	-
MoO ₃	-	-	13.0
<u>Support</u>	Amorphous silica-alumina	Amorphous silica-alumina	Crystalline silica-alumina
<u>Form</u>	1/16-inch cylindrical extrudate	1/12-inch cylindrical extrudate	1/8-inch cylindrical extrudate

The effectiveness of these catalysts for the hydrocracking reaction depends on the acidity function provided by the silica-alumina support. This limits how much nitrogen the hydrocracker feed can contain, since the nitrogen can be converted to ammonia or other basic nitrogen compounds which neutralize the acid sites. Therefore, a feed with a relatively low nitrogen content was required, to avoid rapid catalyst deactivation which could obscure true activity differences.

For these screening runs, hydrocracking charge stock was prepared by severely hydrotreating a raw coker gas oil similar to that used in the screening of hydrotreating catalysts. The raw coker gas oil, prepared by commercial-scale delayed coking of Athabasca bitumen at Sun Co.'s tar sands plant in Alberta Province, was hydrotreated in two steps. The first pass was in continuous mode, commercial sized equipment at the plant site. The second pass was in batch equipment at the ARD facility in Marcus Hook. Properties of the hydrotreated coker gas oil were:

Gravity, °API	30.6
Distillation range by ASTM D1160	
°F 0__vol.%	
5	320
50	590
95	730
Aromatics, wt.%	40
Nitrogen content, ppmw	6.4
Sulfur content, ppmw	13

For the hydrocracking activity runs, end-of-run weight balances and product distributions were determined. Because aviation turbine fuel was the principal objective, the degree of conversion of that fraction of the feed which is higher boiling than the principal product (about 490°F for JP-4), to material boiling at temperatures less than the target 490°F, could be taken as a measure of the activity of the catalyst at any set of operating conditions.

Runs were made over each catalyst at 2,000 psig and over a 60°F span in reaction temperature. Figure 4 illustrates the trends observed. The conversion level increased regularly with reaction temperature (the data for Catalyst B at the highest temperature were estimated, because the gas sample was lost). The two nickel-tungsten on amorphous silica-alumina materials were comparable in terms of hydrocracking activity, while the experimental Catalyst C showed a distinct activity advantage. The difference exceeds 100°F, well above the estimated test precision range.

Catalyst selection based solely on relative hydrocracking activities could be misinformed. The material being hydrocracked --in this case, the >490°F fraction-- must also yield products in the desired boiling range. For JP-4, this would be the nominal 120° to 490°F range. Product distributions for the three test catalysts are illustrated in Figure 5 as a function of conversion. All three catalysts gave about the same proportion of light products (the initial to 120°F fraction) to turbine fuel components (the 120° to 490°F fraction). Table 3 lists projected product distributions at a uniform 60% conversion level. The differences are small and the three are considered to have provided equivalent product distributions.

The above results were reviewed with the project technical officer and the decision made to use the high activity experimental catalyst (Catalyst C) in the subsequent continuous mode studies.

Conditions: Batch reactor
60cc catalyst
360cc hydrotreated coker gas oil feed
2,000 psig
4 hours reaction time

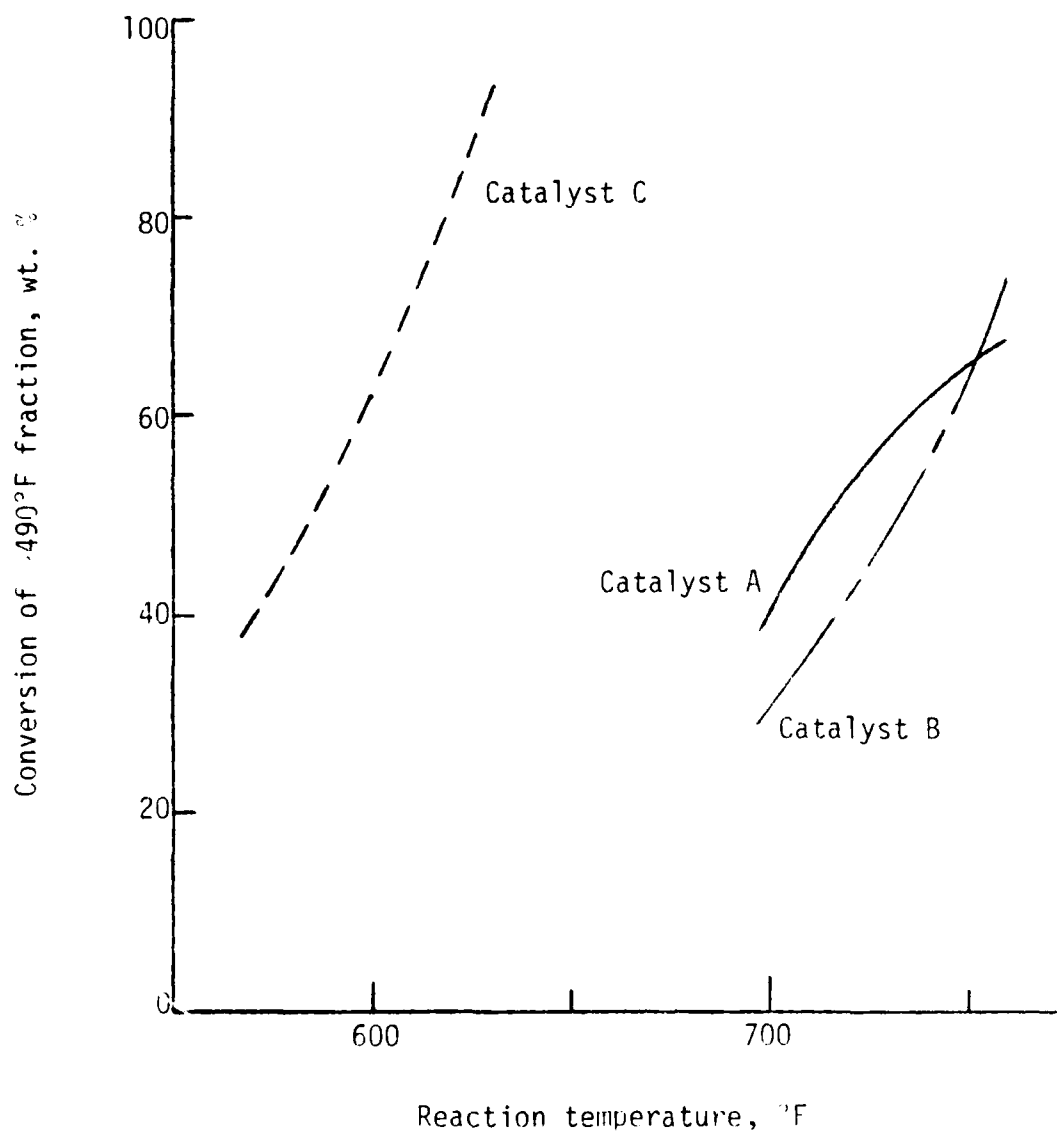


FIGURE 4 COMPARISON OF HYDROCRACKING CATALYST ACTIVITIES

Conditions: Batch reactor
60cc catalyst
360cc hydrotreated coker gas oil feed
2,000 psig
4 hours reaction time

Note: letters designate catalyst code

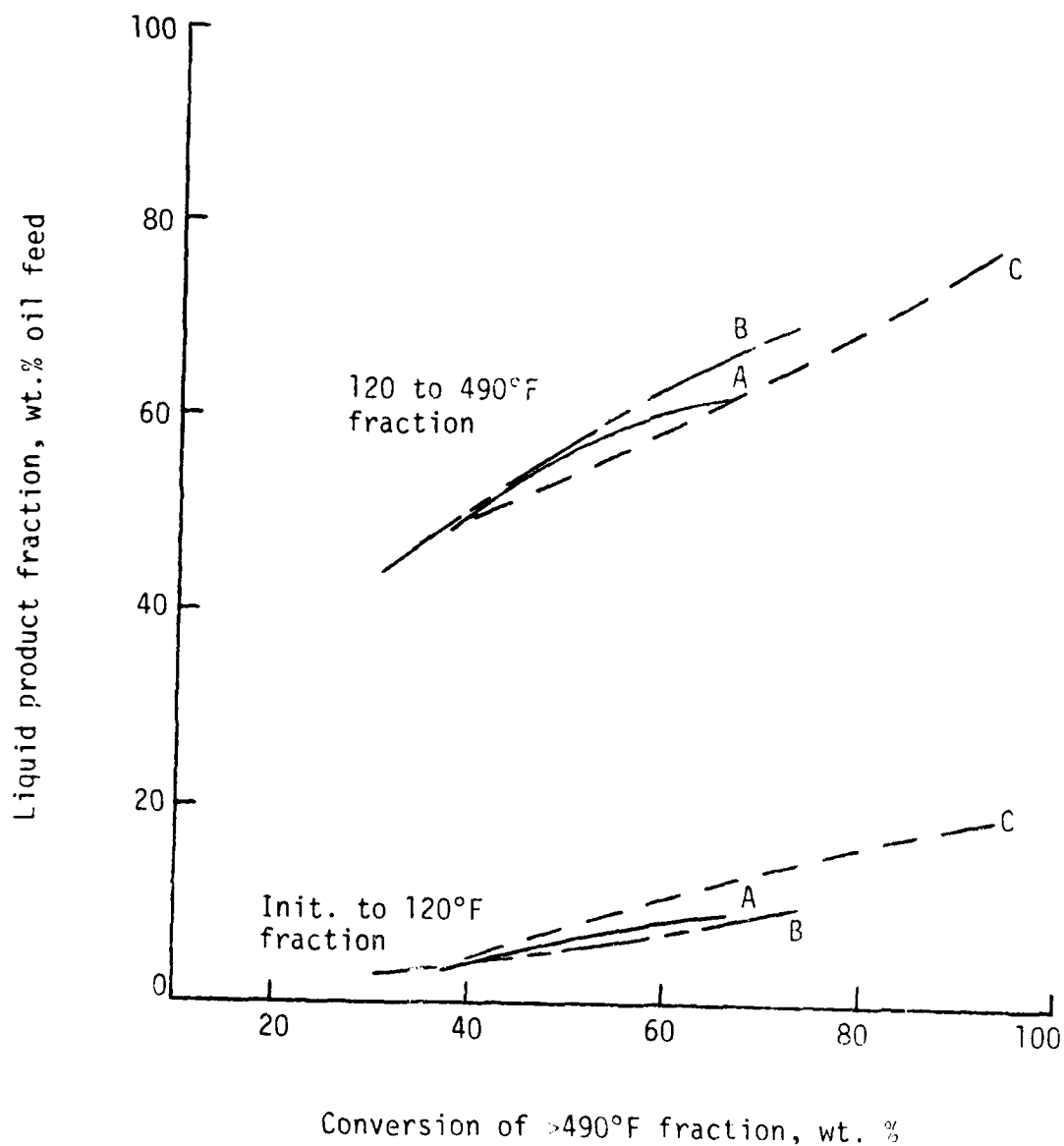


FIGURE 5 HYDROCRACKING PRODUCT DISTRIBUTIONS

TABLE 3

PRODUCT DISTRIBUTION FOR BATCH HYDROCRACKING RUNS

<u>Catalyst code</u>	<u>A</u>	<u>B</u>	<u>C</u>
<u>Catalyst type</u>	Ni-W on amorphous Si-Al	Ni-W on amorphous Si-Al	Ni-Mo on crystalline Si-Al
<u>Feedstock</u>	Hydrotreated coker gas oil		
<u>Reaction conditions</u>			
Temperature, °F(1)	735	745	593
Pressure, psig	←-----2000-----→		
Time, minutes	←-----240-----→		
Catalyst/oil, volume	←-----1:6-----→		
<u>Product distribution, wt%(2)</u>			
Hydrogen	0.5	0.7	0.7
Dry gas (C ₁ -C ₃)	0.3	0.4	0.2
Butane (C ₄)	0.2	0.3	0.5
Pentane (C ₅)	0.1	0.1	0.1
Liquid fractions(3)			
Init-120°F	8.8	6.9	10.8
120°-490°F	60.8	62.7	58.8
490°F-btms	30.4	30.4	30.4

(1) Requirement (est'd.) for 60% conversion

(2) Based on 60% conversion of >500°F fraction via simulated distillation

(3) Estimated, via simulated distillation

SECTION IV

HYDROVISBREAKING

1. Introduction

In the process concept under study, bitumen or heavy crude residue is upgraded in a hydrovisbreaking operation, prior to more intensive downstream refining to produce finished fuels. Hydrovisbreaking consists of exposing the feed to appropriate combinations of time, temperature and pressure, converting much of the non-distillable portion of the feed to distillable material. The conversion is largely thermal, although it may be advantageous to include small amounts of an additive to control the amount and location of insoluble material produced during the conversion.

The studies to be described in this section had several objectives:

- evaluation of the effect of principle process variables
- definition of significant feedstock effects
- production of sufficient quantities of hydrovisbroken liquids to support the downstream studies.

Were it not for the third objective, the studies could be conveniently carried out in small-scale hardware such as rocker bombs or stirred reactors. The resultant close control of reaction conditions and accounting for reactants and products would permit detailed comparison of the variables under study. However, to produce the volume of products desired, larger scale equipment was necessary, which scale-up was accompanied by some loss in precision.

2. Procedure

Hydrovisbreaking experiments were carried out in a batch mode, using a 10-gallon capacity stainless steel autoclave. The high pressure vessel was equipped with variable speed agitator, heating jacket, thermowell, and

cooling coil. The large mass of the reactor and contents limited flexibility of the operation. For example, constraints on electrical and thermal loads resulted in heat-up times ranging from 6 to 12 hours, a significant factor when evaluating reaction times of 1 to 2 hours. Further, removal of the top flanged head of the reactor required several hours of shop mechanic time to break all connections and the vessel seal. In addition, all broken joints were susceptible to hydrogen leakage, on subsequent start-up. It was clearly impractical to remove the vessel head after each run. Without this visual inspection, the amount of liquid heel (in the absence of a bottom drain, vessel contents were pressured out via dip tube) or adherent solids remaining in the autoclave could not be determined.

In a typical experiment, about five gallons of liquid feed were pumped from a heated drum into the autoclave. The change in gross weight of the drum, pump, and contents provided the amount charged. While the heating mantle was energized, the autoclave was pressure tested, then pressured and depressured several times with hydrogen to displace nitrogen remaining after the pressure test. Heating, with maximum agitation, was continued. The initial hydrogen pressure of 500 psig was adjusted as required, when thermocouples indicated the contents were approaching reaction temperature. During the designated reaction span of 1, 2, or 5 hours, additional hydrogen was admitted to the autoclave as necessary to maintain reaction pressure. At the conclusion of the reaction period, the autoclave and contents were cooled, aided by steam in the internal coil. When the system had cooled to 300 to 400°F, the vapor space was slowly depressured through a cold water condenser and gas metering/sampling system. Since the gas composition was continually changing during the venting process, periodic gas samples were taken for analysis. After all pressure was released, the vapor space was purged with nitrogen and the liquid removed. Liquid pressured out via the dip tube was combined with light condensate trapped out in the vent gas system, and the combined liquids submitted for analysis. Weight balances were calculated from the liquid charge plus hydrogen metered into the system and compared to liquid recovered plus gas exiting via the vent gas system.

For the 49 separate autoclave runs comprising the study, weight balance results were:

<u>Weight balance</u> <u>closure, wt%</u>	<u>Number of</u> <u>runs</u>
± 5	39
±10	5
±15	2
>15	3

The weight balance calculations did not take into account any solids formed and left behind in the autoclave after the reaction products were discharged. Periodically, the autoclave top was removed for inspection and any accumulated solids removed. Since the several preceding runs (usually about six) had been made at varying conditions, attribution of the weight of solids for weight balance purposes was not attempted.

No coke-suppressing additive was included with the feed other than what might be present by natural occurrence. For Phase III work, one or more of the additives mentioned in the literature will be assessed for effectiveness in reducing coke deposits for the particular feed to be evaluated.

Hydrovisbroken liquid was tested for total nitrogen content, sulfur content, distillation characteristics and specific gravity. The remaining liquid product was composited, according to the feed being processed but independent of conversion level, and retained for use in subsequent portions of the program.

3. Feedstocks

Four feedstocks were hydrovisbroken in this manner in the 10-gallon autoclave. Two were bitumens --one from Kentucky (Kensyntar) and one from Utah (Sunnyside)-- and two were >650°F fractions from two heavy crude oils --Hondo Monterey and San Ardo, both from California. Pretreatment of the feeds in preparation for the hydrovisbreaking operation was described in Section II of this report.

Physical and chemical characteristics of the four hydrovisbreaking feedstocks are listed in Table 4. All have relatively low API gravities, ranging from 8.5° API for the San Ardo residue to 11.9° API for the Sunnyside bitumen. Each feed includes about 50 volume percent material distillable at temperatures below 1,000°F. At 0.8 weight percent, nitrogen content of the two bitumens is fairly high; the San Ardo residue is especially noteworthy with 1.4 weight percent nitrogen. The Hondo Monterey residue, on the other hand, stands out with its high sulfur content. More detailed chemical and structural analyses of these materials are possible, and would have been appropriate if achieving a better understanding of the reactions occurring during hydrovisbreaking were one of the stated objectives of this activity. However, in the absence of such a goal, the feed inspections were limited to those capable of describing generally the nature of the materials in use and the extent of their conversion.

Both the analytical data and process results with the Sunnyside bitumen were scattered and inconsistent. From certain inspections, it appeared some kerosene diluent may have been left in the bitumen after the feedstock preparation step. Repeat analyses left the discrepancies unresolved. Finally, it was concluded that the inventory of diluent-stripped bitumen was fairly non-uniform and that data and/or results may not be representative.

4. Results

The hydrovisbreaking studies were of a scouting nature, with limited investigation of the effects of the major process parameters such as reaction time, reaction temperature, and overall pressure. Since the upgrader functions primarily as a molecular weight reducer, emphasis was on conversion of non-distillable to distillable material.

Due to the high thermal inertia of the autoclave system, heat-up and cool-down times frequently exceeded by a considerable degree the nominal reaction times of 1 or 2 hours. By extending reaction times at low temperatures to 5 hours, a time effect could be discerned which was masked

TABLE 4
HYDROVISBREAKING FEEDSTOCKS

<u>Type</u>	<u>Heavy crude atmospheric residue</u>		<u>Bitumen</u>	
<u>Source</u>	<u>Hondo Monterey</u>	<u>SanArdo</u>	<u>Kensyntar</u>	<u>Sunnyside</u>
<u>Physical properties</u>				
Gravity, °API	8.9	8.5	9.8	11.9
Sp. gravity, 60/60°F	1.0078	1.0107	1.0014	0.9868
Distillation, °F at ___ % (by ASTM D1160)				
IBP	476	577	508	214
5	703	699	590	449
10	736	743	630	505
20	819	796	713	587
30	903	830	801	782
40	962	-	898	877
50	-	-	980	-
EP	962	-	1005	906
	049%		056%	045%
Carbon residue, wt%	13.3	11.7	9.5	13.2
<u>Chemical analysis by weight</u>				
Nitrogen, total, %	0.98	1.39	0.85	0.79
Sulfur, %	6.25	2.31	1.49	0.32

at shorter reaction times. Data for processing the Hondo Monterey feed at 2,500 psig illustrate this effect:

<u>Temperature, °F</u>	<u>Time hours(1)</u>	<u>Conversion of >1000°F, Vol. %</u>
725	1	44
	2	44
	5	72
750	1	58
	2	63
	5	78

(1) excludes heating and cooling cycle

Thus, the inertial effect has obscured the doubling of the nominal 1-hour reaction time, although the expected trend toward higher conversion with longer time is evident in the 5-hour runs.

Overall reaction pressure was varied between 1,500 and 2,500 psig for several feeds and combinations of operating conditions. On first consideration, the presence of the additional hydrogen in the vapor space above the liquid might be expected to result in more rapid removal of heteroatoms, such as nitrogen and sulfur. Comparison of six pairs of runs made at either 1,500 or 2,500 psig with three different feeds (the Utah bitumen is excluded) is shown below:

<u>Property of recovered liquid</u>	<u>Average of six runs (1) at 1,500 psig at 2,500 psig</u>		<u>Ratio, (x100)</u>
Sulfur content, wt%	2.273	2.282	99.6
Nitrogen content, wt%	1.272	1.300	97.9
Conversion of >1000°F, vol%	52.5	39.1	134.2

(1) four-run average for nitrogen content

For these matched pairs of runs, heteroatom removal was unaffected by the reaction pressure imposed, whereas conversion of the non-distillate portion of the liquid feed was sharply reduced at the higher total pressure.

The reduction in liquid conversion level at the higher pressure is consistent enough to be real, and unanticipated. One possible explanation is that the additional hydrogen and/or total pressure during the reaction inhibits the cracking reactions by preventing the formation and escape of the lower molecular weight volatile products. It remains to be seen whether similar effects would be observed in a continuous operation, compared to the static environment of the autoclave. If the pressure effect were to persist, however, other operating parameters such as temperature or residence time could be readily adjusted to achieve the desired conversion level. The critical question, then, would be whether the change in pressure exerts a significant effect on either product distribution or product quality.

In these studies, the most significant variable by far was the reaction temperature. At otherwise uniform reaction conditions, higher temperatures resulted in:

- higher estimated hydrogen consumption
- lower specific gravity (i.e. higher API gravity) of the recovered liquids
- modest reduction, but only at the higher temperature levels, in the total nitrogen content of the liquid products
- regular reduction in the sulfur content of the recovered liquid
- higher content of distillable liquid in the recovered liquid product

These trends are illustrated, for series of autoclave runs performed at a nominal 2-hour reaction time, 2,500 psig reaction pressure, and temperatures from 700°F to 800°F, in Figures 6 and 7.

The above patterns generally hold, regardless of which feed is being processed. The data for the Sunnyside bitumen exhibit some scattering, which as noted earlier may result from non-uniformities in that particular sample. Some feedstock effects are readily apparent --higher nitrogen content or sulfur content feeds yield higher nitrogen or sulfur content liquid products. In addition, the bitumen feeds appear to be slightly more refractory, i.e., at comparable reaction conditions, the liquid products

Conditions: 2,500 psig
2 hours (nominal) reaction time
feed - as shown

○—○ Hondo Monterey >650°F fraction
□—□ San Ardo >650°F fraction
△—△ Kensyntar bitumen
◇—◇ Sunnyside bitumen

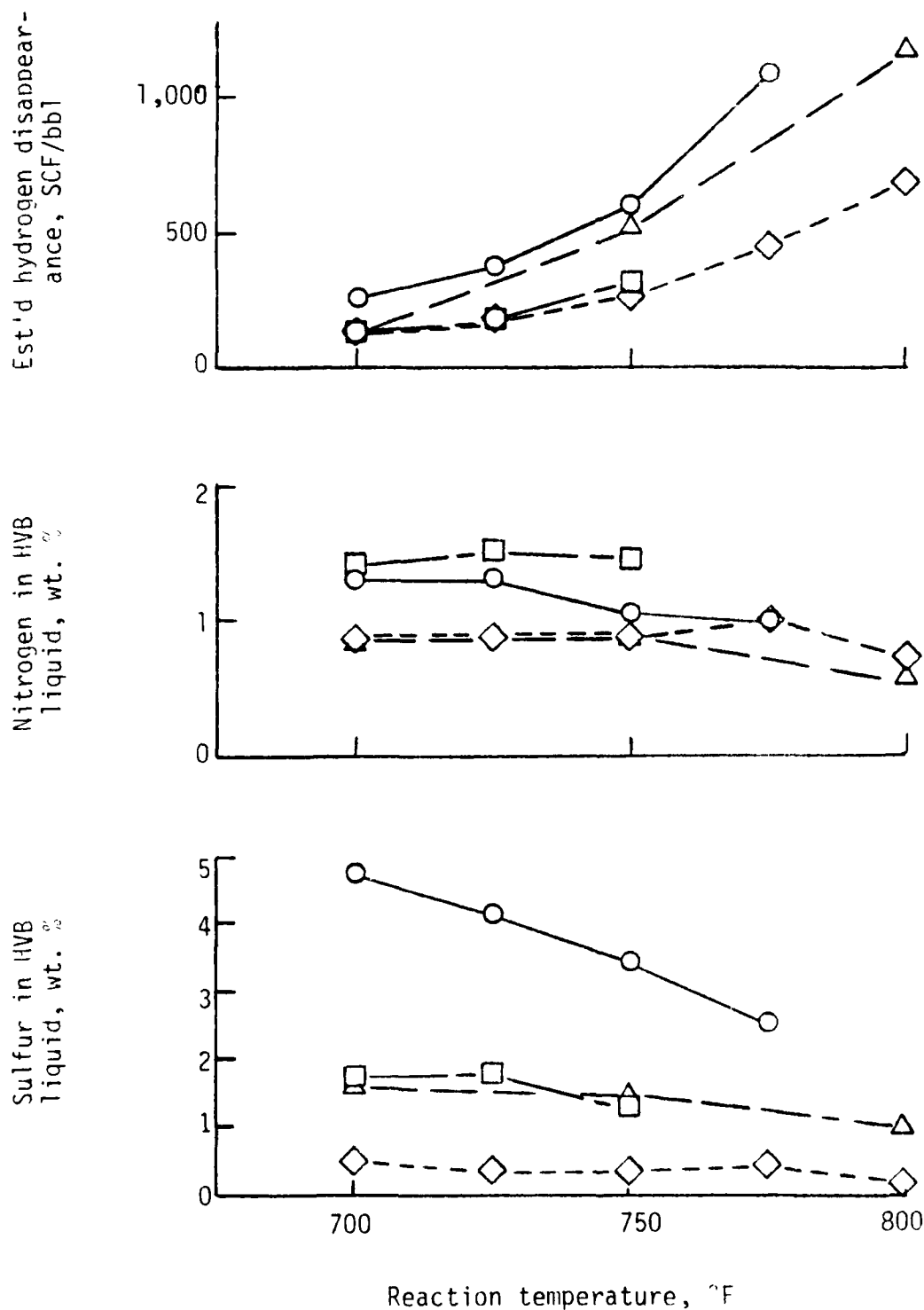


FIGURE 6 TEMPERATURE EFFECTS IN BATCH HYDROVISBREAKING

Conditions: 2,500 psig
2 hours (nominal) reaction time
feed - as shown

- Hondo Monterey >650°F fraction
- San Ardo >650°F fraction
- △—△ Kensyntar bitumen
- ◇—◇ Sunnsyside bitumen

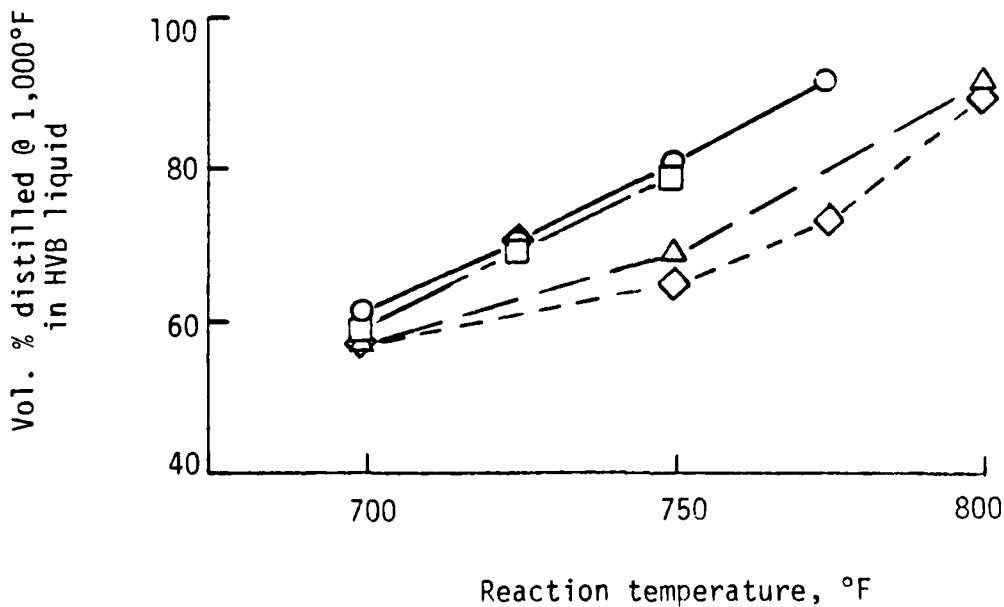
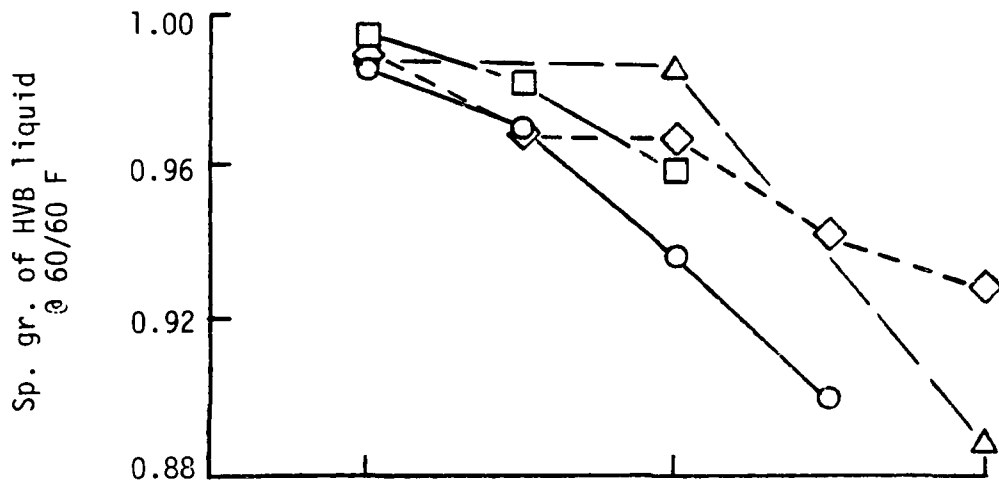


FIGURE 7 TEMPERATURE EFFECTS IN BATCH HYDROVISBREAKING

from processing the bitumens contain somewhat less distillable material than do those from processing the heavy crude residues.

Product distributions were determined for a series of runs for each feedstock over a wide range of conversion levels. Where feasible, the data were obtained from 2-hour runs at 2,500 psig. In a few cases, it was necessary to include runs at slightly different conditions, in order to cover adequately the desired conversion range.

Figures 8 through 11 summarize these results for, respectively, the Hondo Monterey and San Ardo heavy crude residues and for the Kensyntar and Sunnyside bitumens. For each feed, the yields of C₁-C₃ gaseous products increase with conversion. Except for the Sunnyside bitumen feed, which had relatively low sulfur content, the amount of hydrogen sulfide in the vented gas increased regularly with conversion level. Net hydrogen, i.e. hydrogen added minus hydrogen recovered, indicated increasing amounts consumed as conversion increased.

Liquids produced were expressed as C₄ to 500°F light oil fraction and a 500° to 1,000°F heavy oil fraction. The light oil yield was determined by adding (mathematically) the equivalent volume of any C₄'s, C₅'s or C₆'s in the vented gas to the volume of IBP to 500°F calculated from the overall material balance and a vacuum distillation (by ASTM method D1160) of the recovered liquid. The 500°F mark was selected because it is close to the upper cut point for JP-4 type fuels. Thus, the yield of light oil liquid approximates that of material in the JP-4 distillation range. The general pattern for all four feeds was a steady increase in the light oil yield with conversion of the >1,000°F fraction, while the heavy oil yield remained steady or tailed off slightly with increasing conversion.

When compared at equivalent conversion levels, the four different feedstocks produced similar product distributions, with the exception of hydrogen sulfide yields, which generally reflected the relative feedstock sulfur levels. As illustrated in Figure 12, the yield patterns for the hydrovisbreaking operation can, therefore, be expressed as bands which

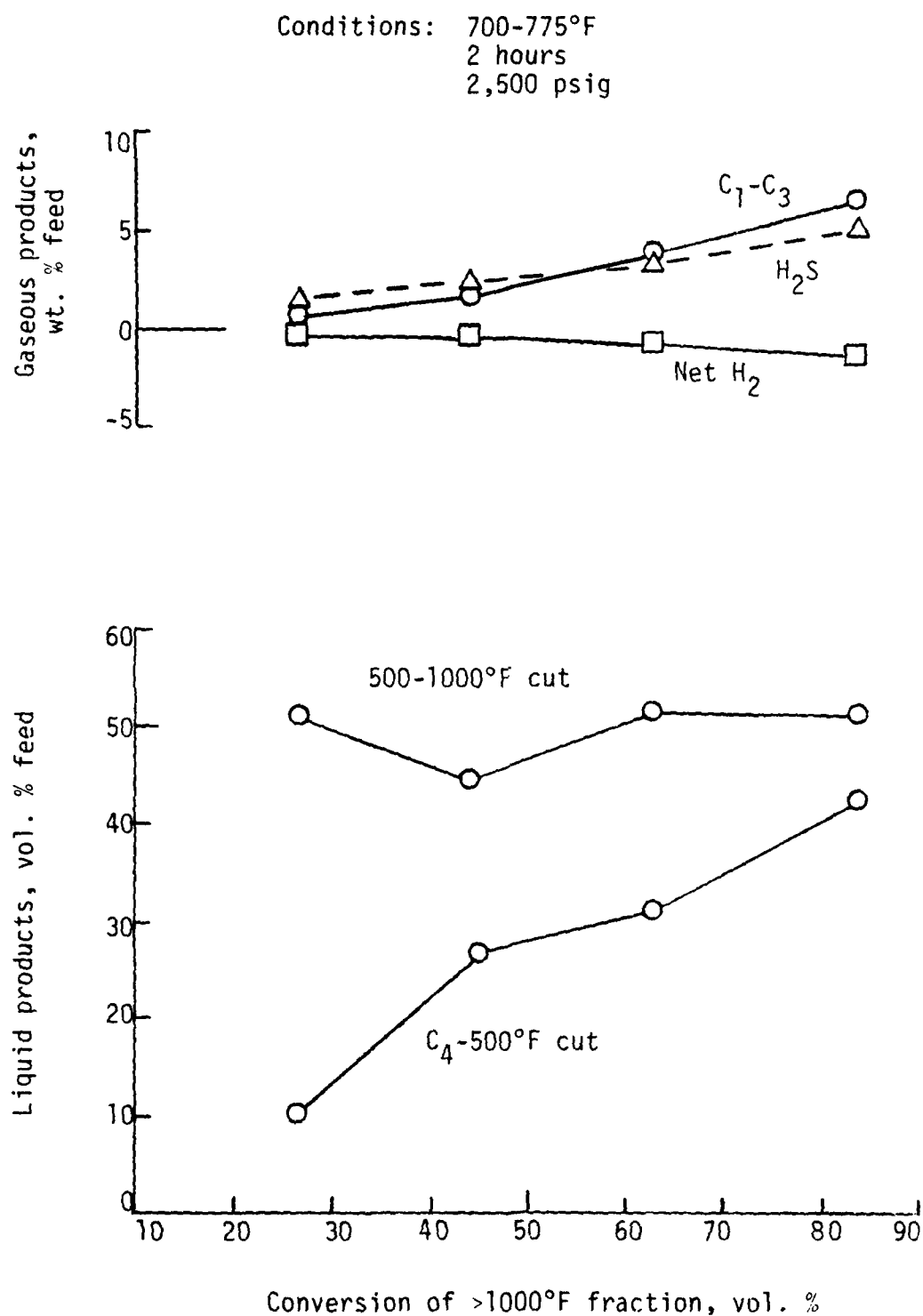


FIGURE 8 BATCH HYDROVISBREAKING OF
HONDO MONTEREY >650°F FRACTION

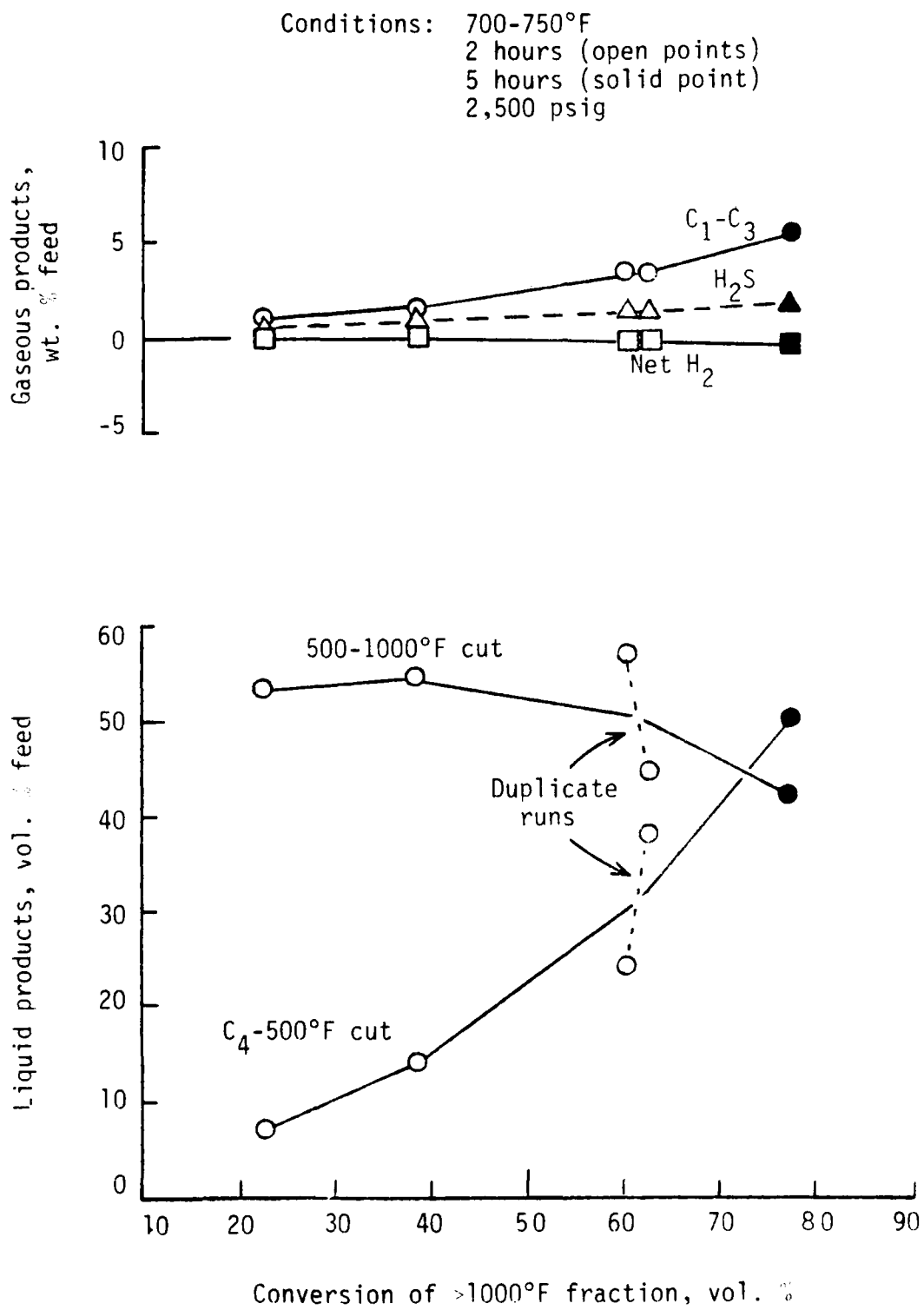


FIGURE 9 BATCH HYDROVISBREAKING OF
SAN ARDO >650°F FRACTION

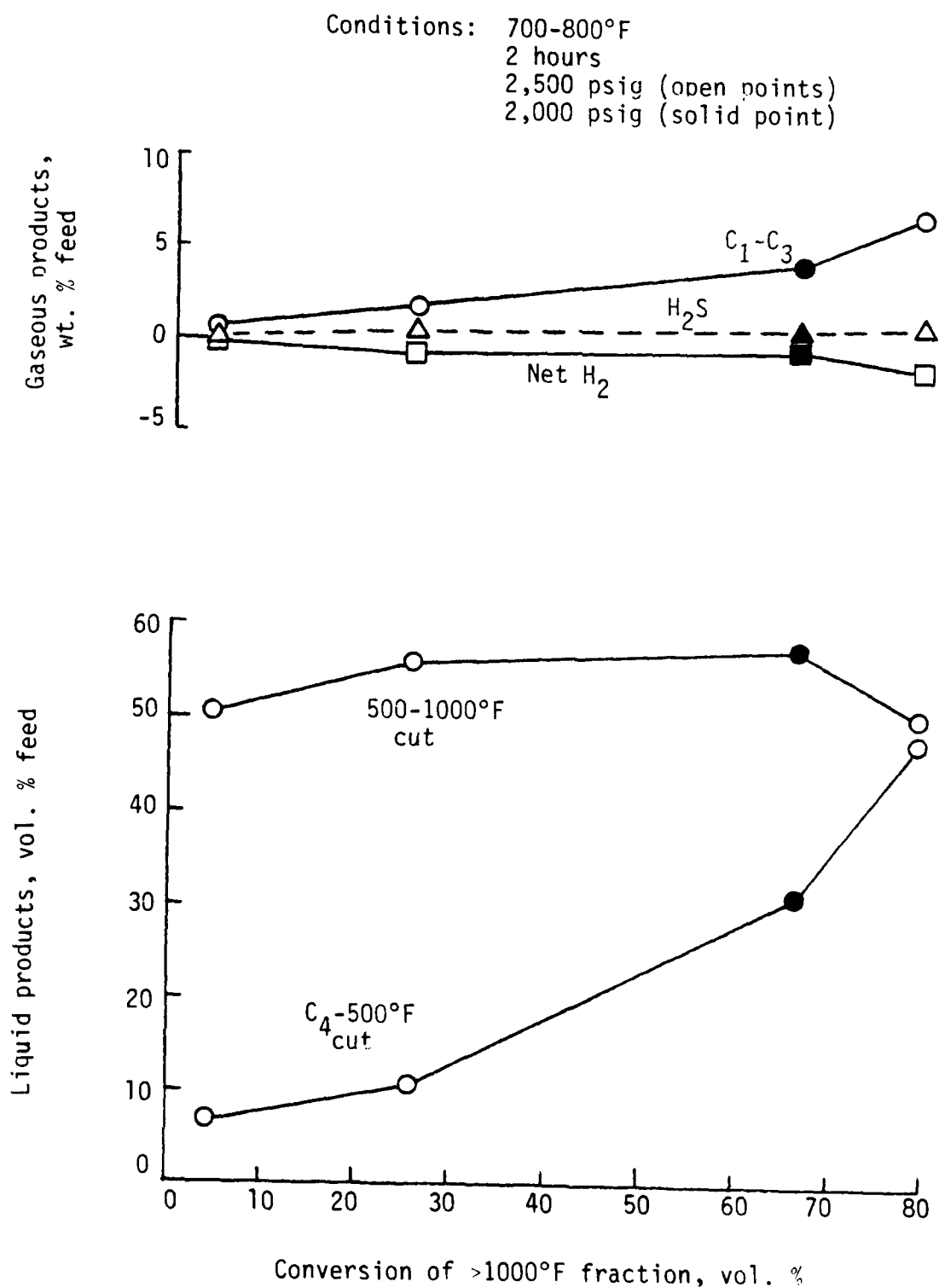


FIGURE 10 BATCH HYDROVISBREAKING OF KENSYNTAR BITUMEN

Conditions: 700-800°F
2 hours
2,500 psig

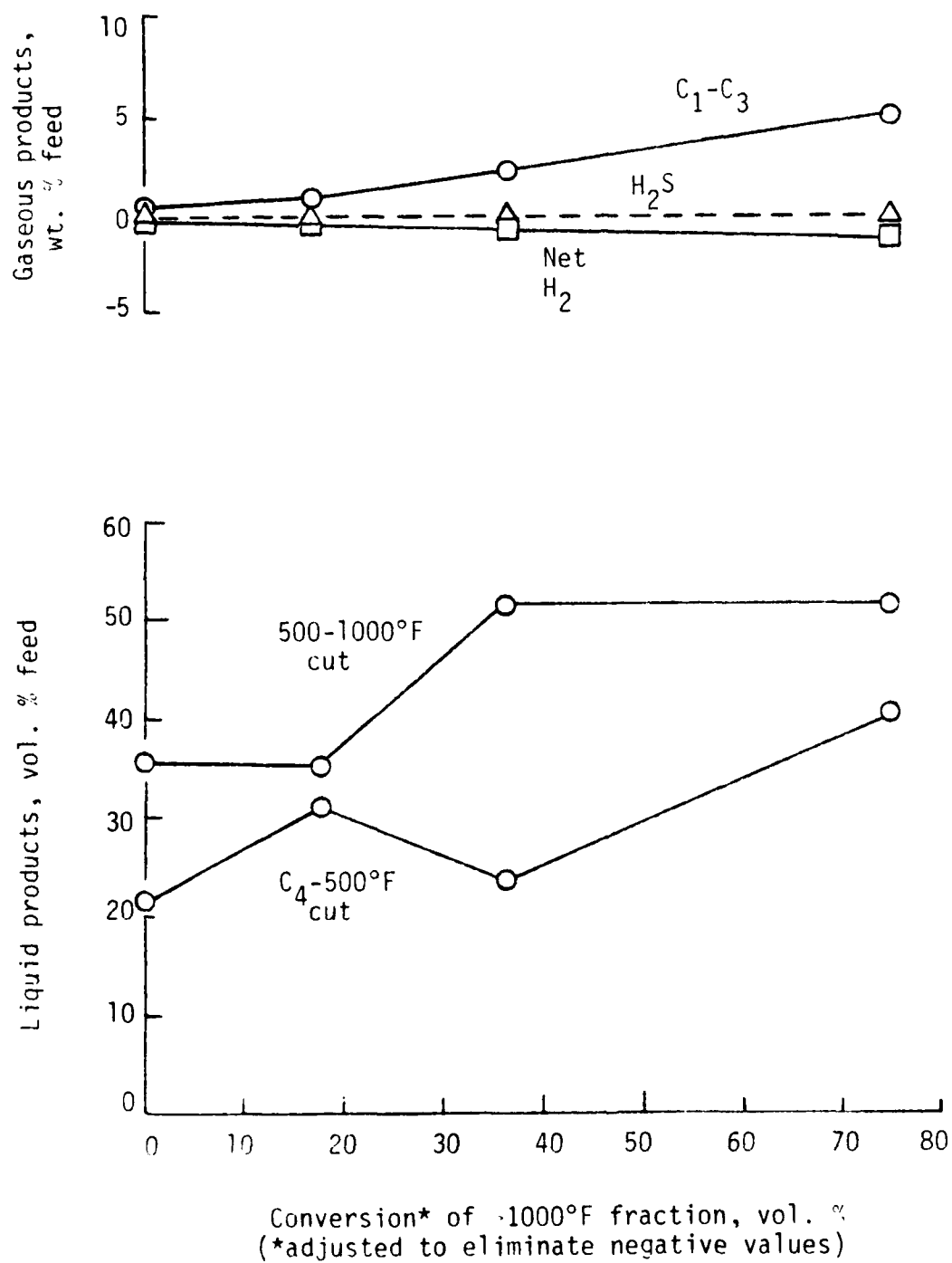


FIGURE 11 BATCH HYDROVISBREAKING OF SUNNYSIDE BITUMEN

Conditions: 700-800°F
2 hours
2,500 psig
four feeds

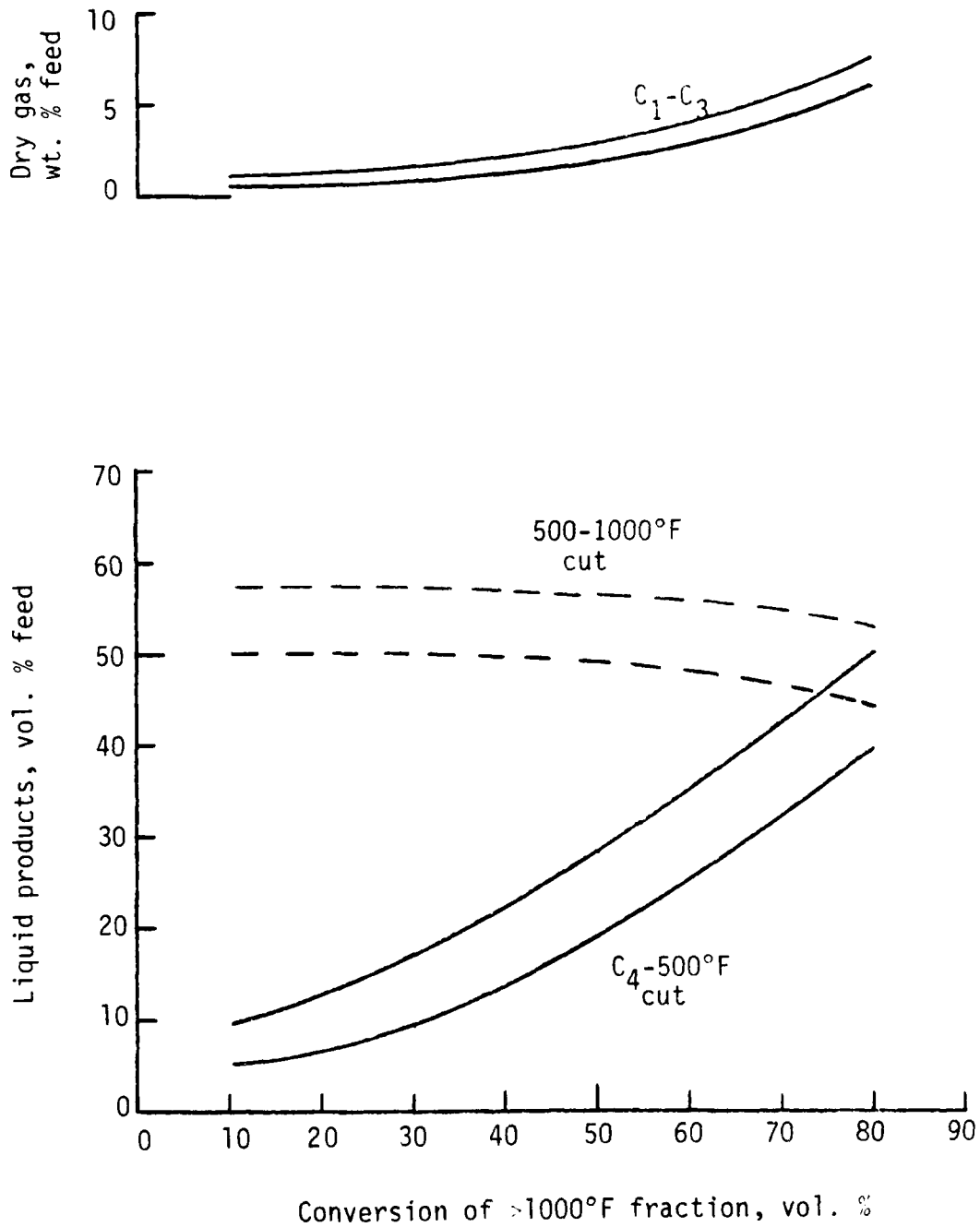


FIGURE 12 GENERALIZED PRODUCT DISTRIBUTION
FOR BATCH HYDROVISBREAKING

represent the product distribution as a function of conversion level, independent of the feed type or source.

The liquids produced during the batch hydrovisbreaking of each feed were retained and composited. These four composites, from 50 to 75 gallons in volume, were then fractionated in laboratory distillation equipment into a naphtha fraction, a vacuum gas oil fraction, and a vacuum residue. The two distillate fractions were used for exploratory studies of the refining processes, to be described next.

SECTION V

HYDROTREATING

1. Introduction

The dark, high-density hydrovisbreaker effluent required additional refining to produce liquids of aviation turbine fuel quality. That portion of the hydrovisbroken liquid which was already within the appropriate boiling range needed further refining to reduce sulfur, nitrogen and possibly olefins and aromatics, to obtain acceptable fuel stability and combustion characteristics. The larger portion of the hydrovisbroken liquid was higher boiling than the desired range for turbine fuels; it was a candidate for refining by hydrocracking. Before that can take place, however, the heavy distillate must be hydroprocessed to reduce catalyst poisons --principally nitrogen compounds and to a lesser extent sulfur compounds-- to harmless levels. Scouting work on both the naphtha and distillate hydrotreating processes is described in this section.

The above approach results in extensive hydrotreating of the whole distillation range of the hydrovisbroken liquids --excluding the non-distillable residues, of course. It also raises the question whether it is more efficient to hydroprocess the liquids as one, two, or more boiling range fractions. Since this program will not generate the data to supply this answer, the selection of two hydroprocessable streams is based on general experience in related applications.

The objectives of these scouting runs were:

- to define one or more sets of operating conditions to achieve the desired degree of refining for each boiling range class
- to determine the effects of the principal operating parameters
- to identify any feedstock effects, whether by class or source
- to produce sufficient quantities of refined products for a) blending of prototype fuel samples, and b) further process studies of the hydrocracking step, or

- to define operating conditions at which subsequent production runs, if required, could be made to satisfy these two needs.

2. Procedure

Continuous-mode hydrotreating studies were performed over a fixed catalyst bed held within a heated, stainless steel, tubular reactor. Preheated reactants passed across the catalyst bed in a downflow direction. The catalyst bed contained 150 ml of catalyst, diluted with inert material to a 50 volume percent active material, with nominal dimensions of 1 inch in diameter by 22 inches in length. Liquid feed and hydrogen were charged on a once-through basis. Both oil and hydrogen feed rates were adjustable, as were reactor temperature and pressure, to achieve variations in processing severity. Average catalyst bed temperatures were determined from a series of thermocouples within a central well. Liquid from the low pressure receiver was continuously charged to a stripping column for removal of dissolved hydrogen sulfide and light hydrocarbons by countercurrent contacting with inert gas.

The catalyst was a nickel-molybdenum on extruded alumina support -- Catalyst A in the screening studies described in Section III. It showed the highest activity among three candidates in laboratory scale testing for nitrogen and sulfur removal from a bitumen-derived raw coker gas oil. Characteristics of the catalyst included:

<u>Composition, wt%</u>	
NiO	4.0
MoO ₃	19.5
<u>Support</u>	Alumina
<u>Form</u>	Shaped extrudate
<u>Size</u>	~1/16-inch diameter

Catalyst was charged to the reactor and, after successful pressure testing of the system, was pre-sulfided according to the manufacturer's recommendations. Sulfiding was done in a hydrogen atmosphere, charging a mixture of carbon disulfide in kerosene at elevated temperature. After pre-sulfiding, the system was slowly brought to operating temperature while

charging a raw coker naphtha. Operation with the coker naphtha feed continued for about 7 days, until analyses of the product liquid indicated the period of initial high activity had passed and catalyst activity had stabilized.

A series of runs was made with each of four naphtha feeds prepared from the respective hydrovisbroken liquid composites. Following completion of the series of naphtha runs, the operation was converted to a distillate hydrotreating study by changing feedstocks and operating conditions. To save time and costs, the distillate hydrotreating studies were performed over the same load of catalyst that had just been used for the naphtha series.

Descriptions of the four feedstocks used in each of the naphtha and distillate hydrotreating studies are included in the discussions of results which follow.

3. Results of Naphtha Hydrotreating Studies

a. Feedstock properties

Four different naphtha feeds were evaluated. Each was derived from one of the four hydrovisbroken low-quality feedstocks. Two were prepared simply by fractionating the composited liquids from hydrovisbreaking either the Kensyntar bitumen or the Sunnyside bitumen. The other two were derived from the Hondo Monterey crude and the San Ardo crude and consisted of a blend of the straight run naphtha plus the naphtha distilled out of the hydrovisbroken composites. The proportion of straight run to hydrovisbroken naphtha was 40:60 by volume for the Hondo blend and 30:70 by volume for the San Ardo blend.

Table 5 lists properties of the four naphtha feeds. Gravity and distillation range data indicate the Kensyntar-derived naphtha is somewhat lighter than the other three. In terms of heteroatom removal, the naphtha from the Hondo Monterey crude represents the most significant challenge. It has not only the highest nitrogen content, but also contains more than 2 weight percent sulfur.

TABLE 5

NAPHTHA HYDROTREATING FEEDSTOCKS

<u>Source</u>	<u>Hondo Monterey</u>	<u>San Ardo</u>	<u>Kensyntar</u>	<u>Sunnyside</u>
<u>Physical properties</u>				
Gravity, °API	47.5	44.4	52.1	46.8
Sp. gravity, 60/60 °F	0.7905	0.8044	0.7707	0.7936
Distillation, °F at ___%				
(by ASTM D86)				
IBP	122	126	123	128
5	173	174	160	180
10	209	204	180	221
20	268	259	212	306
30	304	302	241	350
40	333	348	268	396
50	354	388	295	416
60	376	414	324	424
70	399	432	360	438
80	423	450	391	442
90	445	468	423	452
95	463	482	443	460
FBP	480	494	460	470
<u>Chemical analysis by weight</u>				
Nitrogen, total, ppm	735	514	239	398
Sulfur, %	2.37	0.92	0.27	0.065
Aromatics, vol.% by FIA	20.7	-	18.8	12.1

b. Experimental approach

Symmetrical experimental designs incorporating two levels of the principal process parameters were performed with the first two feeds, the naphtha blends from the Hondo and San Ardo hydrovisbroken crudes. The variables and levels tested were:

<u>Variables</u>	<u>Low level</u>	<u>High level</u>
Temperature, °F	675	725
Space velocity, hr ⁻¹	0.75	1.25
Pressure, psig	1,250	1,750

One run was also made at the centerpoint condition (i.e., at 700°F, 1.0 hr⁻¹ and 1,500 psig) to indicate the extent of any non-linearities in the observed results. Since heteroatom removal was the primary objective, product inspections were mainly total nitrogen and sulfur contents.

Use of the full 2³ factorial design allows evaluation of the main effects by comparing the arithmetic mean of all runs made at the higher level of the variable in question with the mean of all runs made at the lower level.

c. Hondo Monterey feed

When processing the Hondo naphtha, the following results were obtained for the nine-run set:

<u>Variable</u>	<u>Range</u>	<u>Main effect, ppmw</u>	
		<u>Nitrogen</u>	<u>Sulfur</u>
Temperature, °F	675 to 725°F	+0.16	+ 3.4
Space velocity, hr ⁻¹	0.75 to 1.25	-0.10	-3.0
Pressure, psig	1,250 to 1,750	0.0	-2.1
		<u>Level in product, ppmw</u>	
		<u>Nitrogen</u>	<u>Sulfur</u>
Mean of 8-run set		0.18	2.9
Center point run		0.86	2.0

The effects on product nitrogen and sulfur contents, calculated for the stepwise changes in the indicated process variables, are listed under Main effect. Some of the indicated effects are in the opposite direction than that expected. For example, the means of both nitrogen and sulfur in the product were higher for the four runs at 725°F than for the four at 675°F. Also, the means for both nitrogen and sulfur were lower for the less severe 1.25 space velocity runs. Increased operating pressure, on the other hand, had no effect on product nitrogen content but did lower sulfur content by about two parts per million. For the entire eight-run set, the mean nitrogen content of the products was 0.18 ppmw and the mean sulfur content was 2.9 ppmw. The results for the single center-point condition indicate some inconsistency in the nitrogen data. Whereas the product sulfur content for the center point condition is within the bounds of the eight-run design, the nitrogen content is far outside the range of the set and is invalid. That the center point condition produced a product sulfur content about 1 ppm lower than the mean of the 8-run set may reflect either 1) test repeatability or 2) some non-linearity in the relationship between product sulfur and one or more of the test parameters. In this series, the center point run data suggests the relationship between sulfur content and each process parameter is both non-linear and concaved upward. Of perhaps equal importance, the center point run confirms the direction of the main effects reported above for sulfur content.

For this feed, the main variable effects were quite modest, at <0.2 ppmw nitrogen and ~3 ppmw sulfur. Imposition of larger variations in the process parameters could have enlarged these effects until a portion of the design extended into the undesirable regime and thus defined quantitatively a limiting process severity. This did not occur with the experimental design selected. Nevertheless, for the entire nine run set, the removal of 99.98% or more of the heteroatom content of this feed is believed more than adequate for its utilization as aviation fuel blending stock.

d. San Ardo Feed

The same 2^3 factorial pattern of hydrotreating runs was repeated using the San Ardo naphtha blend. The results are summarized below:

<u>Variable</u>	<u>Range</u>	<u>Main effect, ppmw</u>	
		<u>Nitrogen</u>	<u>Sulfur</u>
Temperature, °F	675 to 725	+0.01	+0.30
Space velocity, hr ⁻¹	0.75 to 1.25	0.0	+0.22
Pressure, psig	1,250 to 1,750	-0.01	+0.10

	<u>Level in product, ppmw</u>	
	<u>Nitrogen</u>	<u>Sulfur</u>
Mean of 8-run set	0.08	0.26
Center point run	0.078	0.10

In this series, the means of the product nitrogen and sulfur contents for the eight-run set were even lower, at 0.08 ppmw and 0.26 ppmw respectively, than for the Hondo naphtha. The magnitude of the main effects was also exceptionally low --essentially nil for nitrogen content and only 0.1 to 0.3 ppmw for sulfur. Again, the direction of some product sulfur main effects is opposite what might be expected. For example, mean sulfur content was slightly higher for the four runs at the higher temperature and for the four runs at the higher pressure.

Nitrogen content for the center point run was consistent with the full factorial results, but the center point sulfur content is outside the range of the eight-run set. The pattern for the entire series suggests that, at removal levels exceeding 99.99% for both nitrogen and sulfur, the fluctuation in the product nitrogen and sulfur contents may well be random variations rather than the result of the indicated imposition of the process variables.

e. Kensyntar feed

The experimental pattern was modified for the two bitumen-derived naphthas, after the product analyses from the Hondo and San Ardo naphthas indicated some relaxation in hydrotreating severity was possible. For the Kensyntar-derived naphtha, a reduced level or 2² factorial experimental design, in which temperature was held constant while space velocity and pressure were varied as in the previous 2³ level designs, was performed.

Following that, additional runs were made at successively decreasing severity levels of a single process variable (e.g., temperature or space velocity) in attempts to define at least one boundary of the acceptable operating range.

The results of the factorial design follow:

<u>Variable</u>	<u>Range</u>	<u>Main effect, ppmw</u>	
		<u>Nitrogen</u>	<u>Sulfur</u>
Temperature, °F	Constant at 675	---	---
Space velocity, hr ⁻¹	0.75 to 1.25	+0.01	-0.035
Pressure, psig	1250 to 1750	+0.01	-0.045
		<u>Level in product, ppmw</u>	
		<u>Nitrogen</u>	<u>Sulfur</u>
Mean of 4-run set		0.07	0.17

As indicated above, the product nitrogen and sulfur levels of the four-run set are extremely low --less than 0.1 and 0.2 ppmw, respectively. The main variable effects determined by comparing sample means are even smaller yet. Again, the hydrotreating appears to have been so effective that the variations in product nitrogen and sulfur are believed principally random effects and not related to the indicated variations in process severity. A center point run was not included, as little additional information appeared likely.

The effect of catalyst bed temperature was briefly explored starting from the least severe of the four runs in the experimental design. The following results were obtained:

<u>Temperature,</u> <u>°F</u>	<u>Pressure,</u> <u>psig</u>	<u>Space velocity,</u> <u>hr - 1</u>	<u>Product analyses, ppmw</u>	
			<u>Nitrogen</u>	<u>Sulfur</u>
675	1,250	1.25	0.08	0.17
650	1,250	1.25	0.10	0.09
625	1,250	1.25	0.08	0.18

The successive reductions in reaction temperature had no consistent and significant effect on nitrogen and sulfur in the hydrotreated liquid products.

A second series of runs investigated the effect of increasing space velocity as a means of reducing severity:

<u>Space velocity,</u> <u>hr⁻¹</u>	<u>Temperature,</u> <u>°F</u>	<u>Pressure,</u> <u>psig</u>	<u>Product analyses, ppmw</u>	
			<u>Nitrogen</u>	<u>Sulfur</u>
1.25	675	1,250	0.08	0.17
2.0	675	1,250	0.09	0.18
3.0	675	1,250	0.08	1.16

In this series, it appears that product nitrogen levels were unaffected, but that sulfur content finally began to respond, as the space velocity increased from 2.0 to 3.0 hr⁻¹.

f. Sunnyside feed

Based on its nitrogen and sulfur contents, which were the lowest of the four naphthas in the program, repeating the original factorial design for the Sunnyside naphtha was expected to reveal little about the limiting condition for successful hydrotreating. Therefore, a series of one-dimensional scans of reaction temperature and space velocity were performed to help approach at least one limiting condition.

A scan of reaction temperature at the least severe condition from the original experimental design was performed:

<u>Temperature,</u> <u>°F</u>	<u>Pressure,</u> <u>psig</u>	<u>Space velocity,</u> <u>hr⁻¹</u>	<u>Product analyses, ppmw</u>	
			<u>Nitrogen</u>	<u>Sulfur</u>
675	1,250	1.25	0.12	<0.1
650	1,250	1.25	0.06	0
625	1,250	1.25	0.05	<0.1

The results indicated the hydrotreating conditions were sufficiently severe to achieve essentially complete removal of both nitrogen and sulfur.

Another temperature scan, at a somewhat less severe space velocity condition, was also performed:

<u>Temperature,</u> <u>°F</u>	<u>Pressure,</u> <u>psig</u>	<u>Space velocity,</u> <u>hr⁻¹</u>	<u>Product analyses, ppmw</u> <u>Nitrogen</u>	<u>Sulfur</u>
675	1,250	2.0	0.07	0.25
650	1,250	2.0	0.08	0.09
625	1,250	2.0	0.01	-

The data again suggest that all conditions attempted were adequate for reduction of heteroatom levels to well below one part per million.

One final scan of hydrotreating temperature at an even higher, and thus less severe, space velocity showed:

<u>Temperature,</u> <u>°F</u>	<u>Pressure,</u> <u>psig</u>	<u>Space velocity,</u> <u>hr⁻¹</u>	<u>Product analyses, ppmw</u> <u>Nitrogen</u>	<u>Sulfur</u>
675	1,250	3.0	0.05	0.04
650	1,250	3.0	0.08	0
625	1,250	3.0	0.11	0.58

The limited supply of hydrovisbroken naphtha prevented additional work; however, the final row of data suggest an approaching rapid rise in product sulfur with additional decreases in hydrotreating severity.

g. Feed comparison

The results of these studies are summarized in Table 6. It lists the heteroatom contents of the four naphtha feeds, and also indicates the least severe set of hydrotreating conditions examined which reduced both the nitrogen and sulfur contents of the naphtha product to less than 1 ppmw. For the two naphthas prepared from the California crudes, the hydrotreating conditions did not encompass a wide enough range to define a limiting severity level, so a strict comparison of the conditions listed for the four feeds is not appropriate. Nevertheless, the trend of the data suggest that hydrotreating severity is reflective of the initial heteroatom content of the naphtha feed.

TABLE 6
SUMMARY OF NAPHTHA HYDROTREATING STUDIES

<u>Feed source</u>	<u>Hondo Monterey</u>	<u>San Ardo</u>	<u>Kensyntar</u>	<u>Sunnyside</u>
<u>Feed properties</u>				
Gravity, °API	47.5	44.4	52.1	46.8
Nitrogen, ppmw	735	514	239	398
Sulfur, ppmw	23,700	9,200	2,700	650
<u>Processing conditions⁽¹⁾</u>				
Catalyst	Nickel-molybdenum on alumina			
Avg. bed temperature, °F	675	675	625	625
Pressure, psig	1,250	1,250	1,250	1,250
Space velocity, hr ⁻¹	1.20	1.29	1.27 ⁽²⁾	3.0
Hydrogen feed, SCF/bbl	6,000	6,000	6,000	6,000
Hydrogen consumed, SCF/bbl	337	364	672	1,099
<u>Results</u>				
Product dist'n, wt.%				
H ₂ S	3.3	1.1	0.2	-
C ₁	-	-	-	0.1
C ₂	0.2	0.1	-	-
C ₃	0.6	0.4	0.3	0.2
C ₄	2.6	1.1	0.7	1.1
C ₅	2.4	1.5	1.5	0.8
C ₆	0.6	0.5	0.5	-
Liquid product	90.3	95.3	96.8	97.8
Product yield, vol.%	92.9	96.2	97.4	97.3
C ₅ ⁺ product, vol.%	96.6	98.7	98.6	98.3
Product properties				
Gravity, °API	52.6	47.5	53.1	45.9
Nitrogen, ppmw	0.09	0.09	0.07	0.11
Sulfur, ppmw	0.30	0.18	0.10	0.58

- (1) Conditions shown represent the least severe operating condition tested, for which satisfactory weight balance data were obtained. The test conditions are not necessarily the limiting conditions which yield acceptable product quality.
- (2) Successful processing also observed at 2.0 hr⁻¹ and 3.0 hr⁻¹, but weight balance data unreliable.

Product distributions for one run from each of the four series are also listed in Table 6. The run conditions selected were those made at the lowest severity level at which satisfactory weight balances were obtained. Although a more effective comparison would be at the least severe operating condition required to produce acceptable product quality from each feed, the experimental designs employed were generally unable to identify this condition. In all cases, product nitrogen and sulfur contents were below 1 ppmw.

Yields of light gas were modest, while yields of C₅+ liquid ranged from about 97 to 99 volume percent. The Honda feed appears to have been more severely processed than the other three, as evidenced by the lowest product yield, highest production of C₅ and lighter, and largest change in liquid API gravity. Although unit operations employing once-through hydrogen lead to erratic hydrogen consumption figures, the two bitumen-derived naphthas apparently gave somewhat higher values than the two feeds from the California crudes.

The preceding discussion concentrated on the heteroatom content of the product naphthas as a measure of hydrotreating effectiveness. There is, however, no simple answer to the question "how much hydrotreating is enough?" As blending components, the naphtha products will constitute only a portion of the finished fuel blend. In addition, product properties or characteristics are largely performance-related specifications. Eventually, experimental programs would have to be developed to address the question, but they would be considerably larger than could be accommodated within this program. It is believed, however, that considerably less severe hydroprocessing than was used here may indeed be adequate.

Hydrotreated naphtha products from each of the four feedstocks were retained and composited, for subsequent use in the blending of prototype fuels to be described in Section VII.

4. Results of Distillate Hydrotreating Studies

a. Feedstock properties

Again, four different feeds were evaluated. Two were blends of straight run distillate with a distillate fraction made by hydrovisbreaking either the Hondo Monterey or San Ardo atmospheric residue. In both cases, the volumetric proportion of straight run to hydrovisbroken distillate was 22:78. The other two distillate feeds were distilled directly from the composited hydrovisbroken Kensyntar and Sunnyside bitumens and contained no straight run material.

Table 7 summarizes properties of the four distillate hydrotreating feeds. That prepared from the hydrovisbroken Sunnyside bitumen contained the least amount of nitrogen and sulfur and would appear to be a relatively easy feed to process. Its low specific gravity was consistent with its somewhat lower end point. The two distillates prepared from the California crudes, on the other hand, are noteworthy for their heteroatom contents. The Hondo distillate, with 3.5 percent sulfur, contained about 15 times more than did the distillate from Sunnyside bitumen. The San Ardo distillate, with over 8,000 ppmw nitrogen, contained 2 to 2-1/2 times more than the bitumen-derived distillates.

b. Experimental approach

Distillate hydrotreating studies were performed in the same reactor system and over the same catalyst loading as were used for the naphtha hydrotreating work. Catalyst temperature, reaction pressure, and liquid space velocity were varied to determine the effect on product quality. In the process scheme being simulated, the hydrotreated distillate product becomes the feed to the jet fuel hydrocracker. To avoid extensive activity loss in the hydrocracking section, the total nitrogen content of the feed to the hydrocracker should be less than about 10-20 ppmw. This range, then, became the target quality for the hydrotreater effluent in these studies. In view of the wide range of distillate feed qualities, a single factorial design was considered less effective for these scouting type studies and was not used.

TABLE 7

DISTILLATE HYDROTREATING FEEDSTOCKS

<u>Source</u>	<u>Hondo Monterey</u>	<u>San Ardo</u>	<u>Kensyntar</u>	<u>Sunnyside</u>
<u>Physical properties</u>				
Gravity, °API	21.3	17.1	18.9	22.8
Sp. gravity, 60/60 °F	0.9260	0.9522	0.9408	0.9170
Distillation, °F at ___%				
(by ASTM D1160)				
IBP	389	310	396	445
5	514	344	502	511
10	556	381	540	528
20	597	396	589	555
30	622	427	632	598
40	662	685	669	658
50	692	725	703	698
60	740	794	744	740
70	786	842	784	774
80	843	908	826	811
90	915	977	882	850
95	964	1000	934	882
FBP	-	-	-	922
<u>Chemical analysis by weight</u>				
Nitrogen, total, %	0.544	0.803	0.421	0.338
Sulfur, %	3.50	1.50	1.20	0.236

Large supplies of highly hydrotreated distillate were required at the conclusion of these studies, to support the hydrocracking process studies which were to follow. To conserve feedstock, process scouting studies were limited in scope, but sustained until at least one set of operating conditions was identified which was capable of achieving the desired product quality.

Hydrotreatment of the distillate fractions represents a more severe operation than that of the naphtha fractions, and retention of catalyst activity becomes a greater concern. Several runs were made periodically during the program at one set of operating conditions with the Hondo feed, to determine if catalyst activity had shifted significantly.

c. Hondo Monterey feed

The effects of average catalyst temperature at 2,000 psig and 0.75 space velocity on nitrogen and sulfur content of hydrotreated Hondo Monterey distillate are illustrated in Figures 13 and 14. The concentration of each decreased steadily as temperature increased from 700 to 750°F. Three separate relationships have been drawn; they represent three different time periods during which the data were generated. The lines marked 33 days indicate results obtained shortly after the hydrotreating operation was switched from naphtha to distillate feed. The other sets of lines at 52 and 57-1/2 days are near, and at the conclusion of the distillate studies. They suggest a large loss in catalyst activity, followed by some recovery. This pattern is unusual and no cause has been determined. It may be significant, however, that the runs made immediately prior to the 52-day activity check runs were with the San Ardo distillate, which had the highest nitrogen content of the four feeds at >8000 ppmw. In addition, the Sunnyside distillate, with the lowest nitrogen content at ~3400 ppmw, was processed between the 52 and 57-1/2 day series. Possible explanations then include a) either some cross contamination of products, or b) an apparent or temporary loss of activity caused by the processing of the high nitrogen feed, which may be at least partly recoverable when lower nitrogen feed is re-introduced. Further studies of catalyst activity retention with feed quality should obviously be part of any expanded programs.

Conditions: Ni-Mo on alumina catalyst
2,000 psig
0.75 hr⁻¹ space velocity
feed - blend of straight run plus
hydrovisbroken gas oils
5,440 ppmw nitrogen

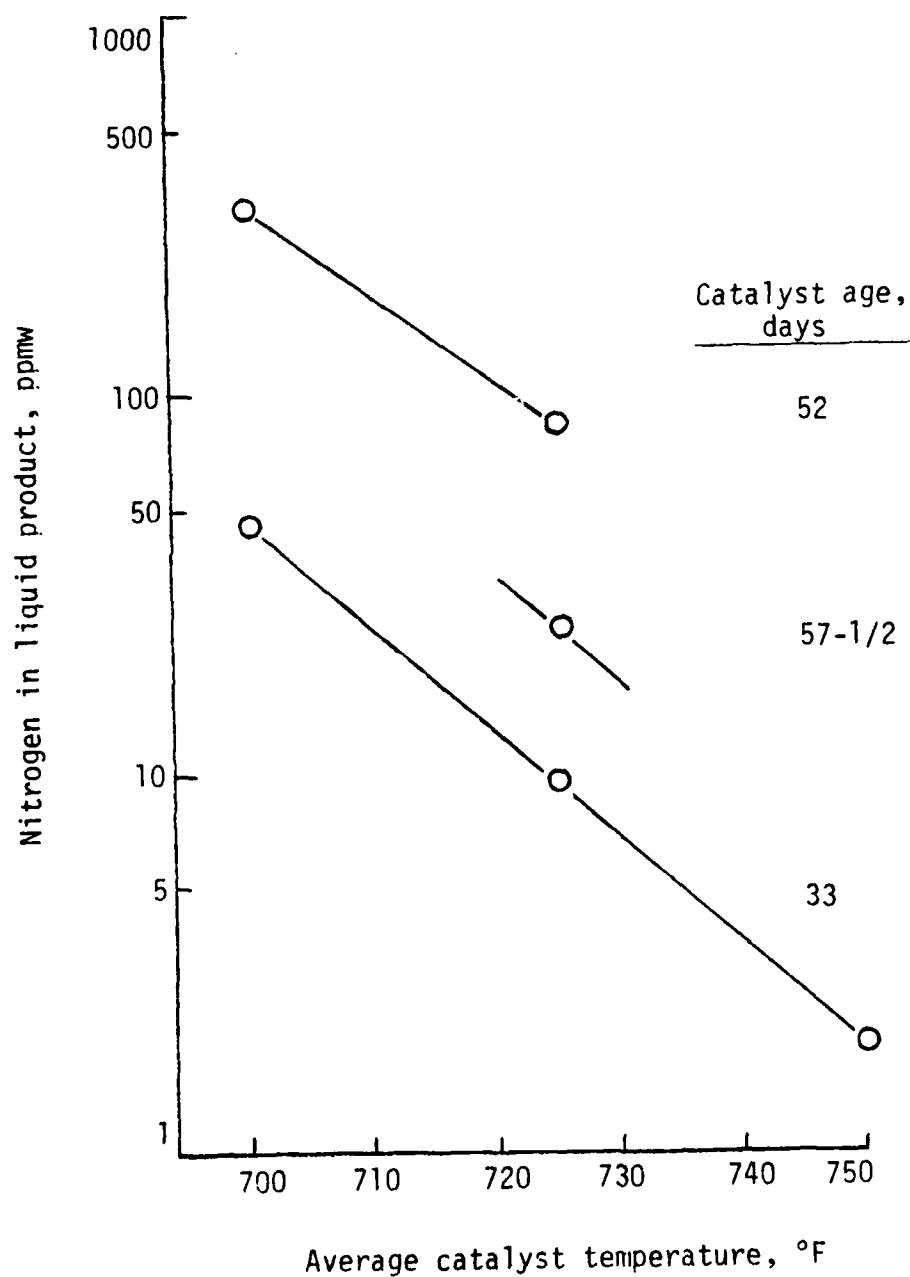


FIGURE 13 HYDROTREATING HONDO MONTEREY DISTILLATE;
CATALYST AGE AND TEMPERATURE EFFECTS

Conditions: Ni-Mo on alumina catalyst
2,000 psig
0.75 hr⁻¹ space velocity
feed - blend of straight run plus
hydrovisbroken gas oils
35,000 ppmw sulfur

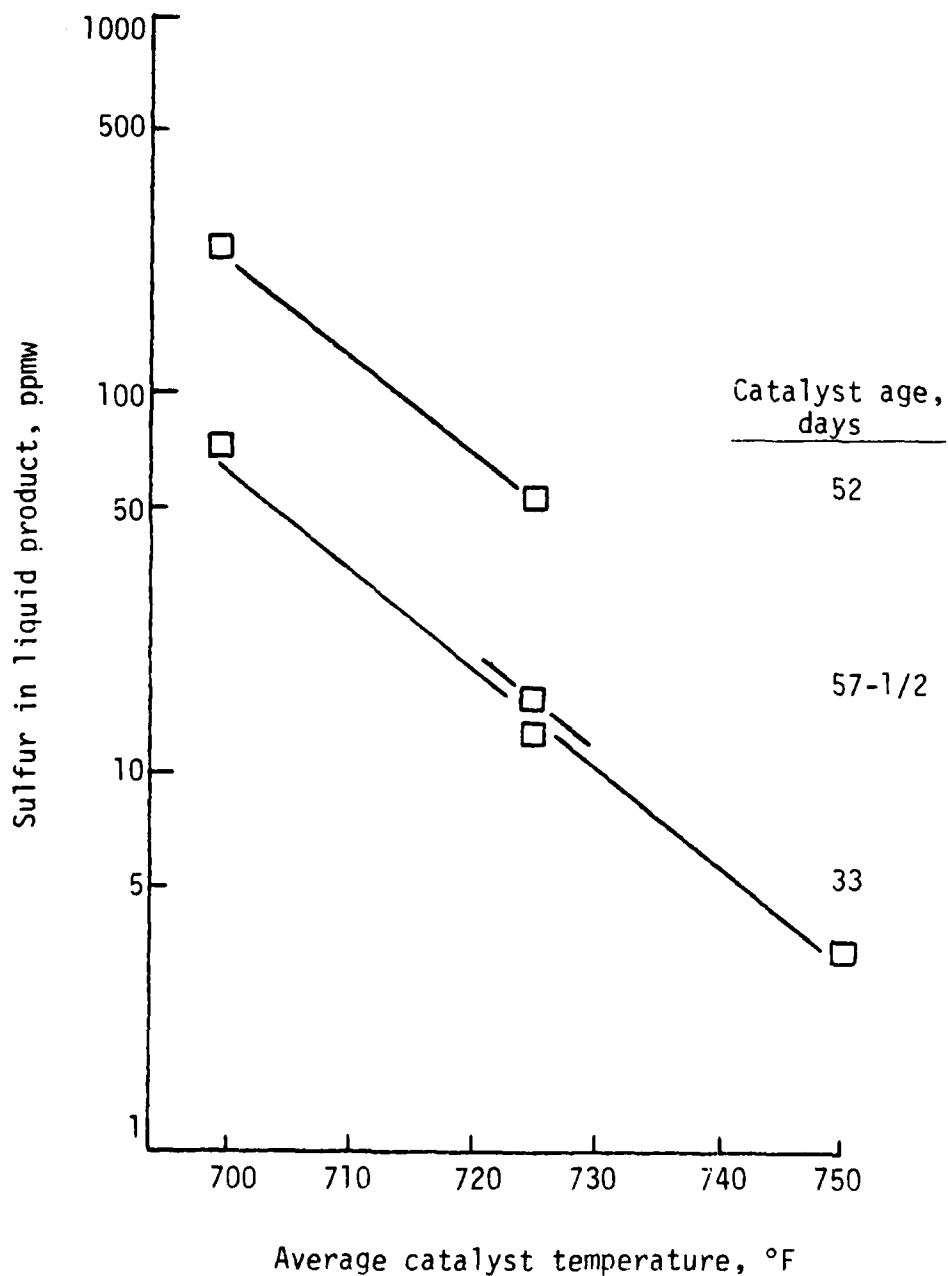


FIGURE 14 HYDROTREATING HONDO MONTEREY DISTILLATE;
CATALYST AGE AND TEMPERATURE EFFECTS

Reduction of the nitrogen content of the Hondo distillate to the 10 to 20 ppm range is readily achieved at these operating conditions over the (relatively) fresh catalyst, provided catalyst is maintained above about 725°F. The 99.6% reduction in feed nitrogen content is accompanied by even more effective removal of sulfur, with product levels approaching the 5-20 ppm range.

d. San Ardo feed

At over 8,000 ppmw, the nitrogen content of the San Ardo distillate blend was the highest of the four distillate feeds to be hydrotreated. As a result, more extensive scouting of process variable effects was necessary to achieve the targeted reduction of nitrogen content to the 10 to 20 ppm range.

Figure 15 illustrates the effect of catalyst temperature on product nitrogen and sulfur contents at 2,000 psig pressure and 0.75 hr⁻¹ space velocity. Over the 700° to 750°F range tested, both nitrogen and sulfur contents decreased regularly with increases in reaction temperature. These conditions were not sufficiently severe to reduce product nitrogen to the desired level, however, so the effects of pressure and/or space velocity were investigated further.

Figure 16 shows the effect of pressure on product quality at 750°F and 0.5 hr⁻¹ space velocity. While both nitrogen and sulfur removal improve at the higher hydrogen partial pressures, the effect on nitrogen content is much more dramatic.

Figure 17 includes the effects of both pressure and space velocity on heteroatom content of the product, and confirms that the San Ardo distillate must be processed at greater than 2,000 psig if unreasonable space velocities are to be avoided. At 2,500 psig and 750°F, operation at about 0.5 hr⁻¹ space velocity or less achieves the desired level of nitrogen in the product.

Conditions: Ni-Mo on alumina catalyst
2,000 psig
0.75 hr⁻¹ space velocity
feed - blend of straight run plus
hydrovisbroken gas oils
8,030 ppmw nitrogen
15,000 ppmw sulfur

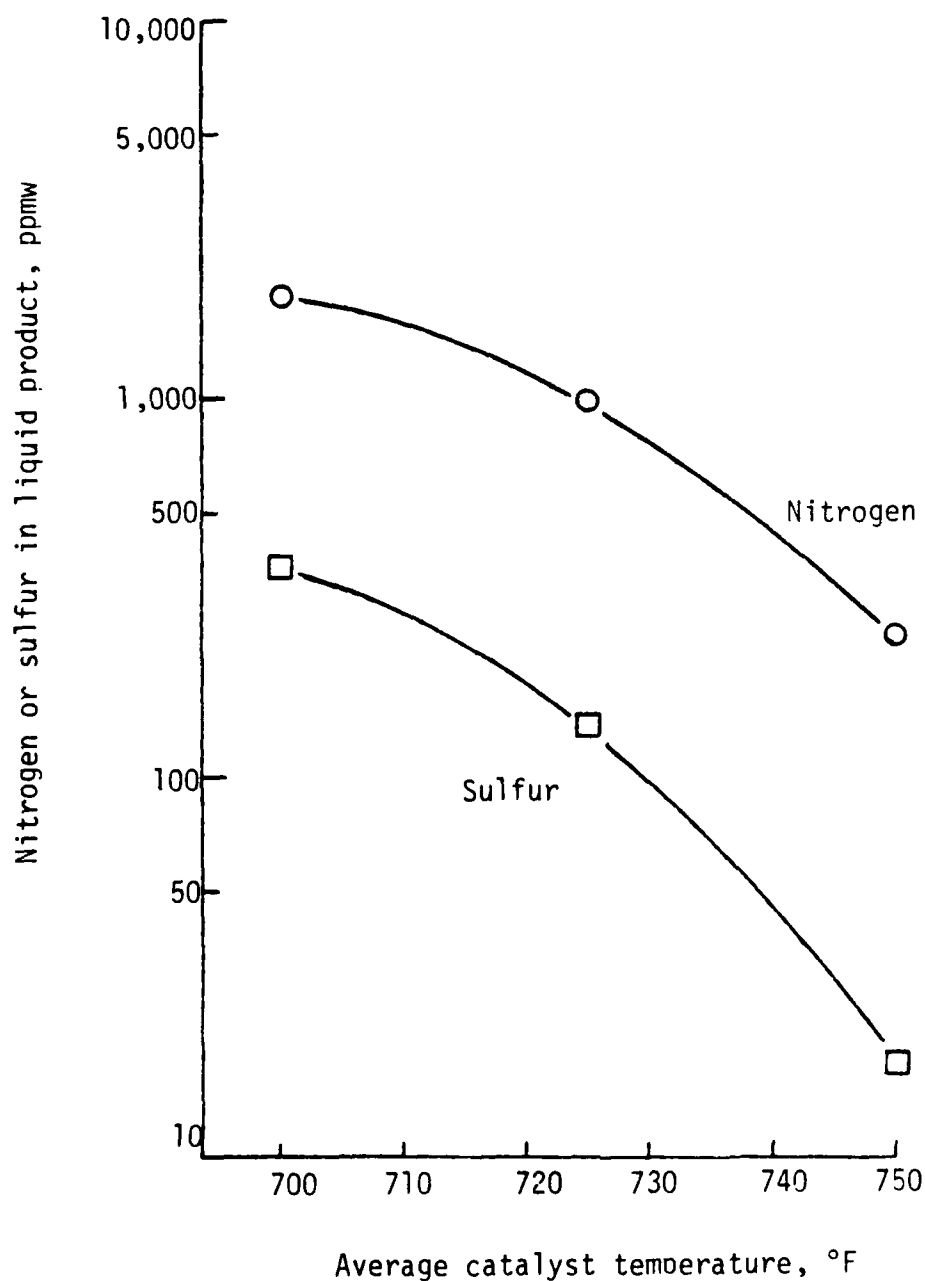


FIGURE 15 HYDROTREATING SAN ARDO DISTILLATE;
TEMPERATURE EFFECT

Conditions: Ni-Mo on alumina catalyst
750°F average bed temperature
0.5 hr⁻¹ space velocity
feed - blend of straight run plus
hydrovisbroken gas oils
8,030 ppmw nitrogen
15,000 ppmw sulfur

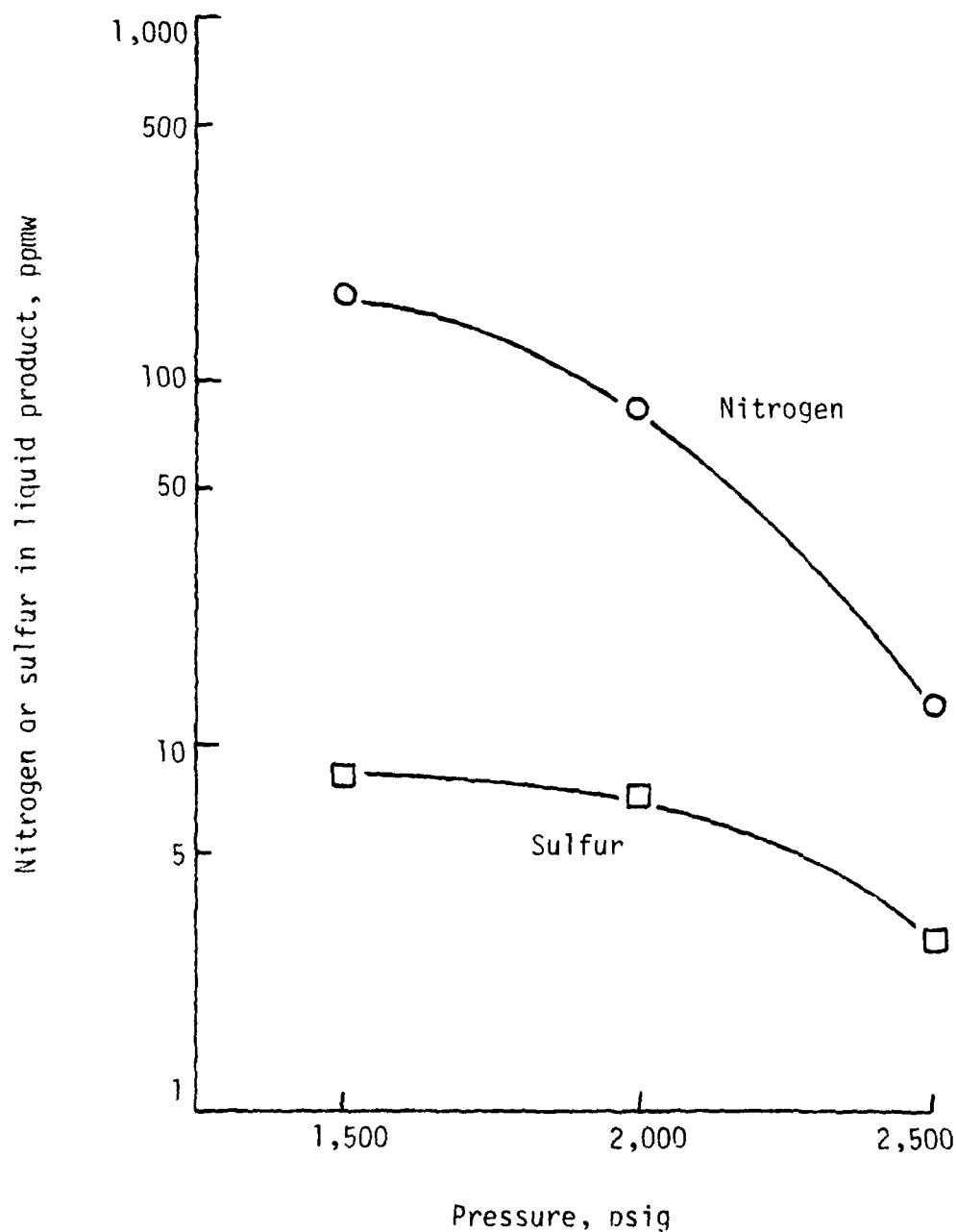


FIGURE 16 HYDROTREATING SAN ARDO DISTILLATE;
PRESSURE EFFECT

Conditions: Ni-Mo on alumina catalyst
 750°F average bed temperature
 2,000 psig (solid points)
 2,500 psig (open points)
 feed - blend of straight run plus
 hydrovisbroken gas oils
 8,030 ppmw nitrogen
 15,000 ppmw sulfur

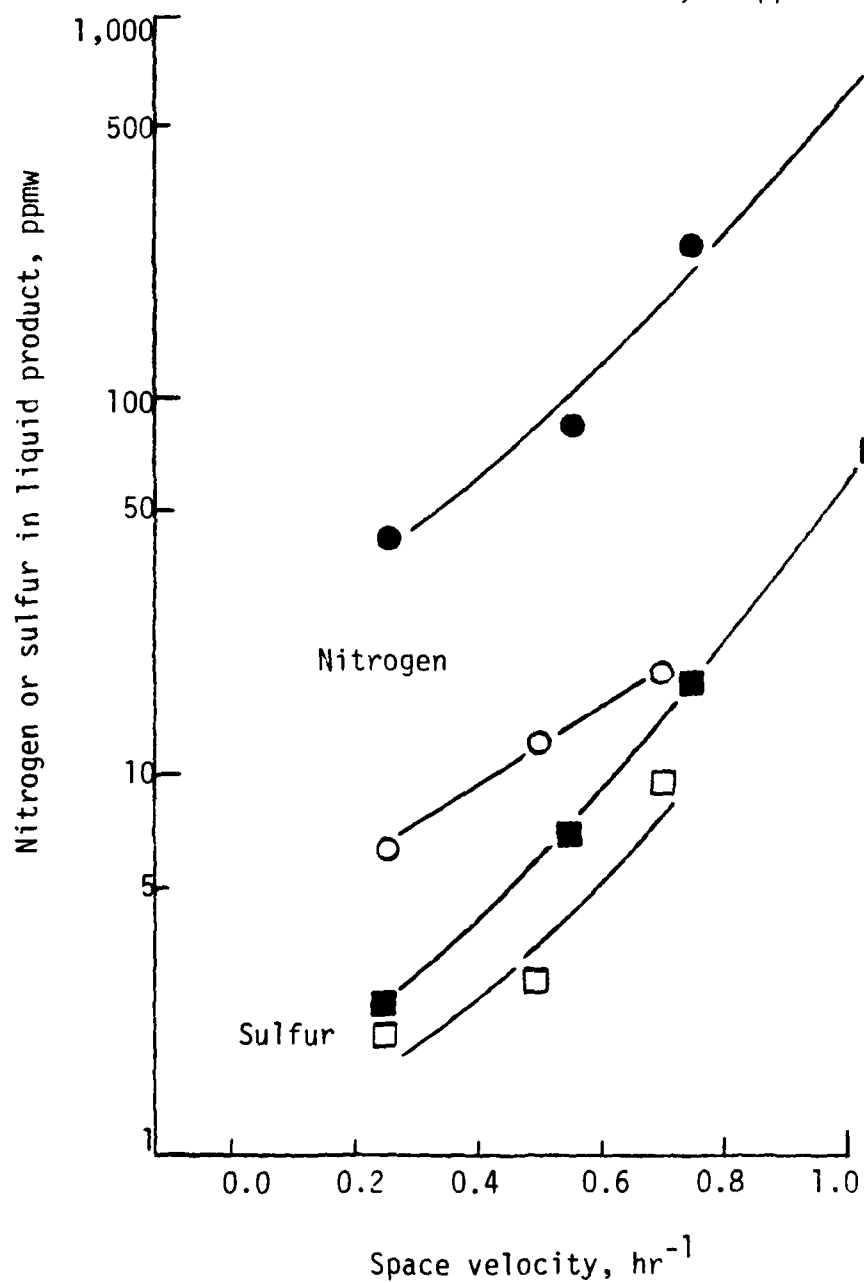


FIGURE 17 HYDROTREATING SAN ARDO DISTILLATE;
 PRESSURE AND SPACE VELOCITY EFFECTS

e. Kensyntar feed

Hydroprocessing the hydrovisbroken distillate from Kensyntar bitumen is illustrated in Figure 18, which shows the effect of catalyst temperature on product nitrogen and sulfur contents at 2,000 psig and 0.65 hr⁻¹ space velocity. Drastic reductions in both nitrogen and sulfur content were realized when temperature was increased to 750°F, resulting in attainment of the target product nitrogen level.

Runs were also made at 1,500 psig to determine if any reduction in processing severity was feasible. Figure 19 presents the data, obtained at 750°F and 1,500 psig and at space velocities from 0.5 to 1.0 hr⁻¹. Product nitrogen and sulfur contents showed the expected decreases with decreasing space velocity. At the most severe condition, nitrogen in the product was again within the desired range. Thus, two combinations of pressure and space velocity were found capable, at 750°F, of reducing nitrogen content to an acceptable level.

f. Sunnyside feed

The distillate prepared from hydrovisbroken Sunnyside bitumen contained the lowest concentrations of nitrogen and sulfur of the four feeds and was therefore expected to require less extreme processing conditions to enable it to meet the product nitrogen target. As illustrated in Figure 20, a quick scan of the temperature effect at 2,000 psig and 0.7 space velocity suggested processing at about 750°F would be required, just as for the other three feeds.

The effect of space velocity is illustrated in Figure 21, indicating a decrease in severity to somewhere between the 0.65 hr⁻¹ and the 1.1 hr⁻¹ levels might be feasible. Results obtained by reducing pressure from 2,000 to 1,500 psig while processing at 0.5 hr⁻¹ space velocity and 750°F are shown in Figure 22. These data also indicate that the decrease in hydrotreating severity can take the form of either lower pressure operation or higher space velocity.

Conditions: Ni-Mo on alumina catalyst
2,000 psig
0.65 hr⁻¹ space velocity
feed - hydrovisbroken gas oil
4,210 ppmw nitrogen
12,000 ppmw sulfur

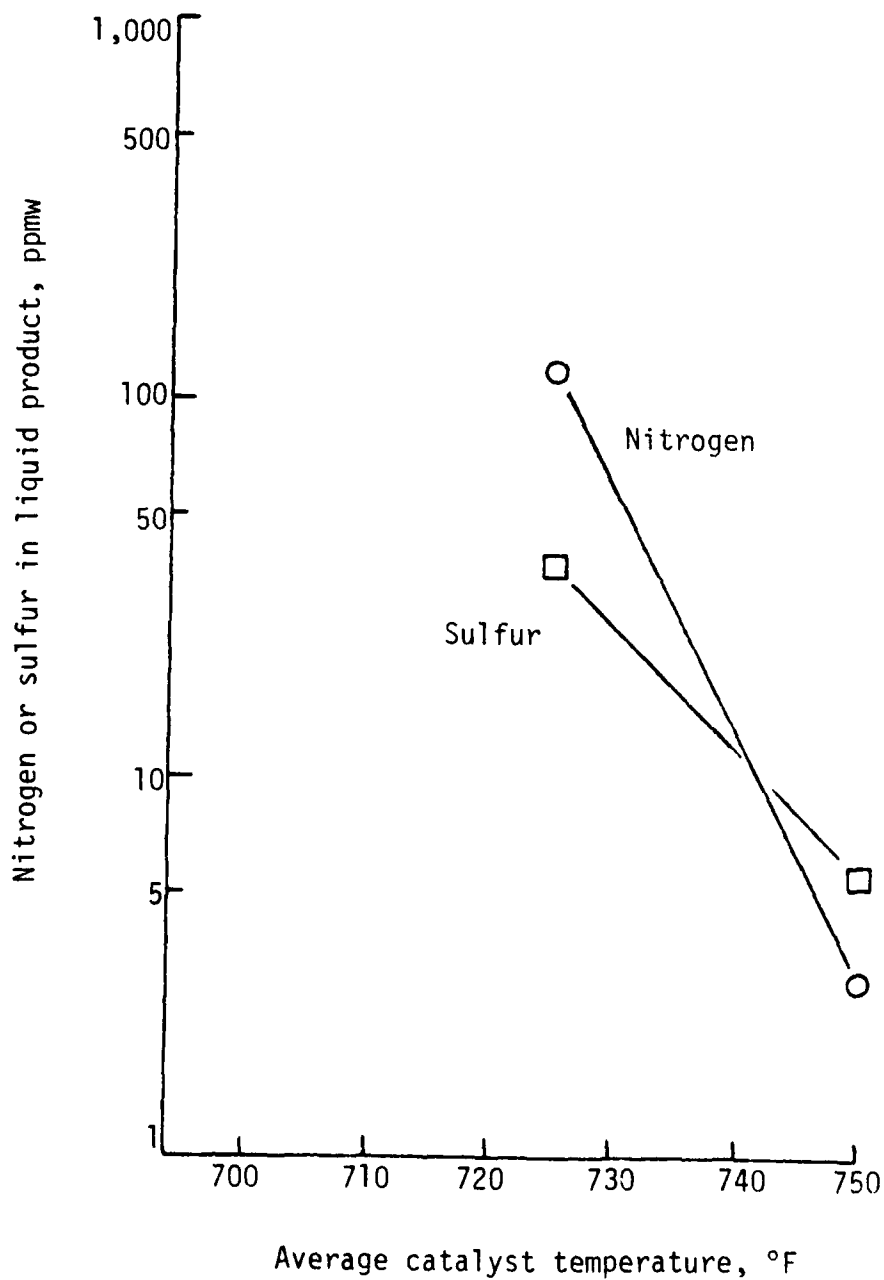


FIGURE 18 HYDROTREATING KENSYNTAR DISTILLATE
TEMPERATURE EFFECT

Conditions: Ni-Mo on alumina catalyst
750°F average bed temperature
1,500 psig
feed - hydrovisbroken gas oil
4,210 ppmw nitrogen
12,000 ppmw sulfur

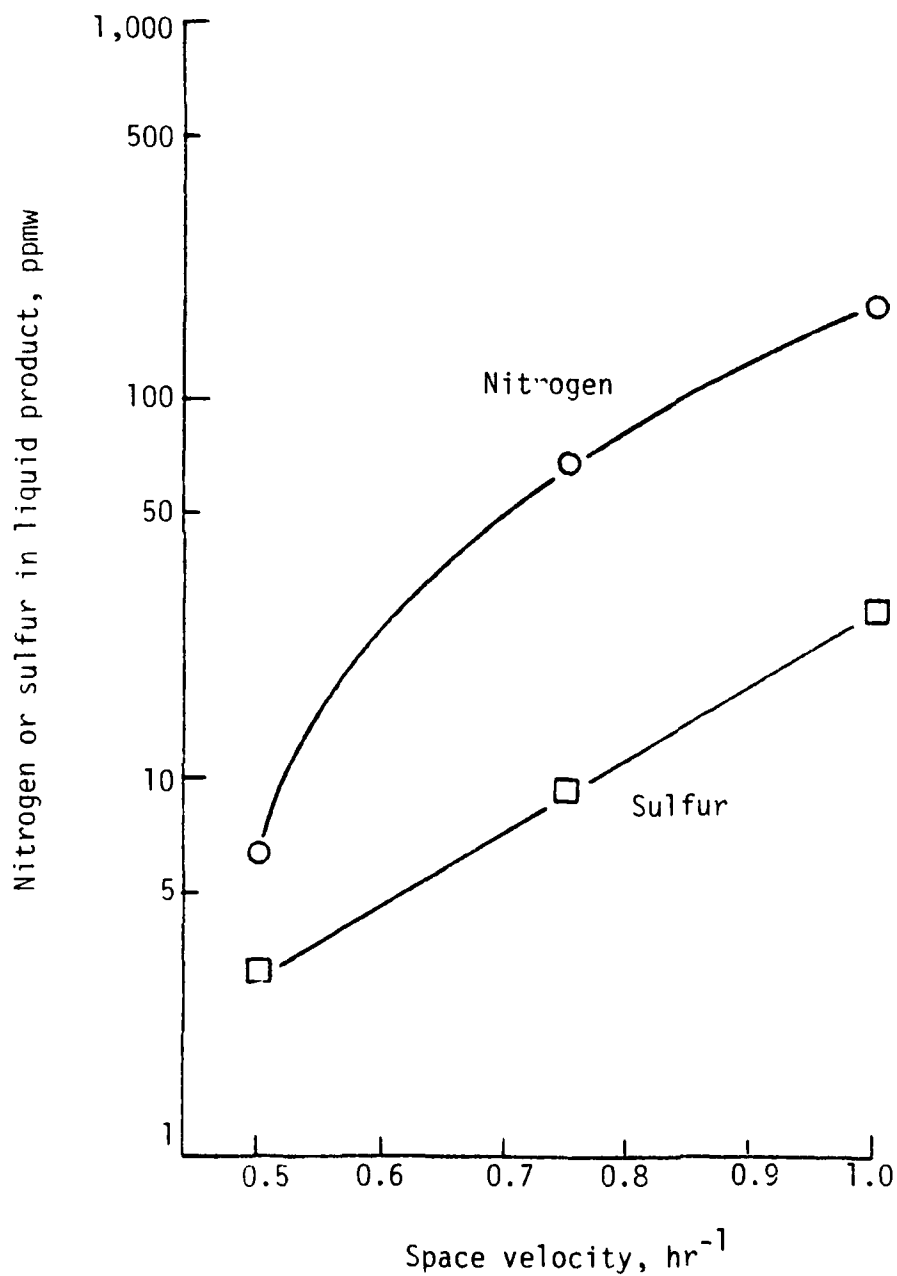


FIGURE 19 HYDROTREATING KENSYNTAR DISTILLATE;
SPACE VELOCITY EFFECT

Conditions: Ni-Mo on alumina catalyst
2,000 psig
0.7 hr⁻¹ space velocity
feed - hydrovisbroken gas oil
3,380 ppmw nitrogen
2,400 ppmw sulfur

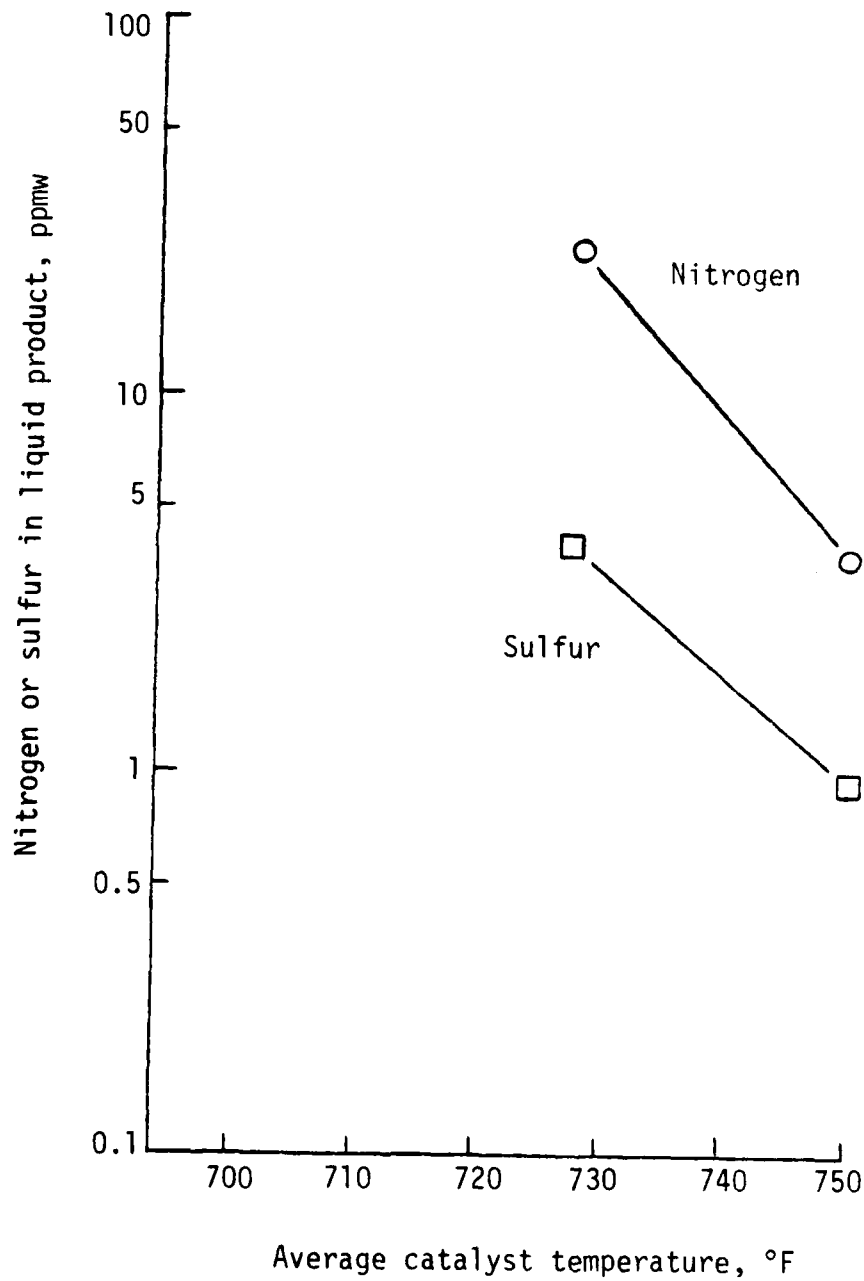


FIGURE 20 HYDROTREATING SUNNYSIDE DISTILLATE;
TEMPERATURE EFFECT

Conditions: Ni-Mo on alumina catalyst
750°F average bed temperature
2,000 psig
feed - hydrovisbroken gas oil
3,380 ppmw nitrogen
2,400 ppmw sulfur

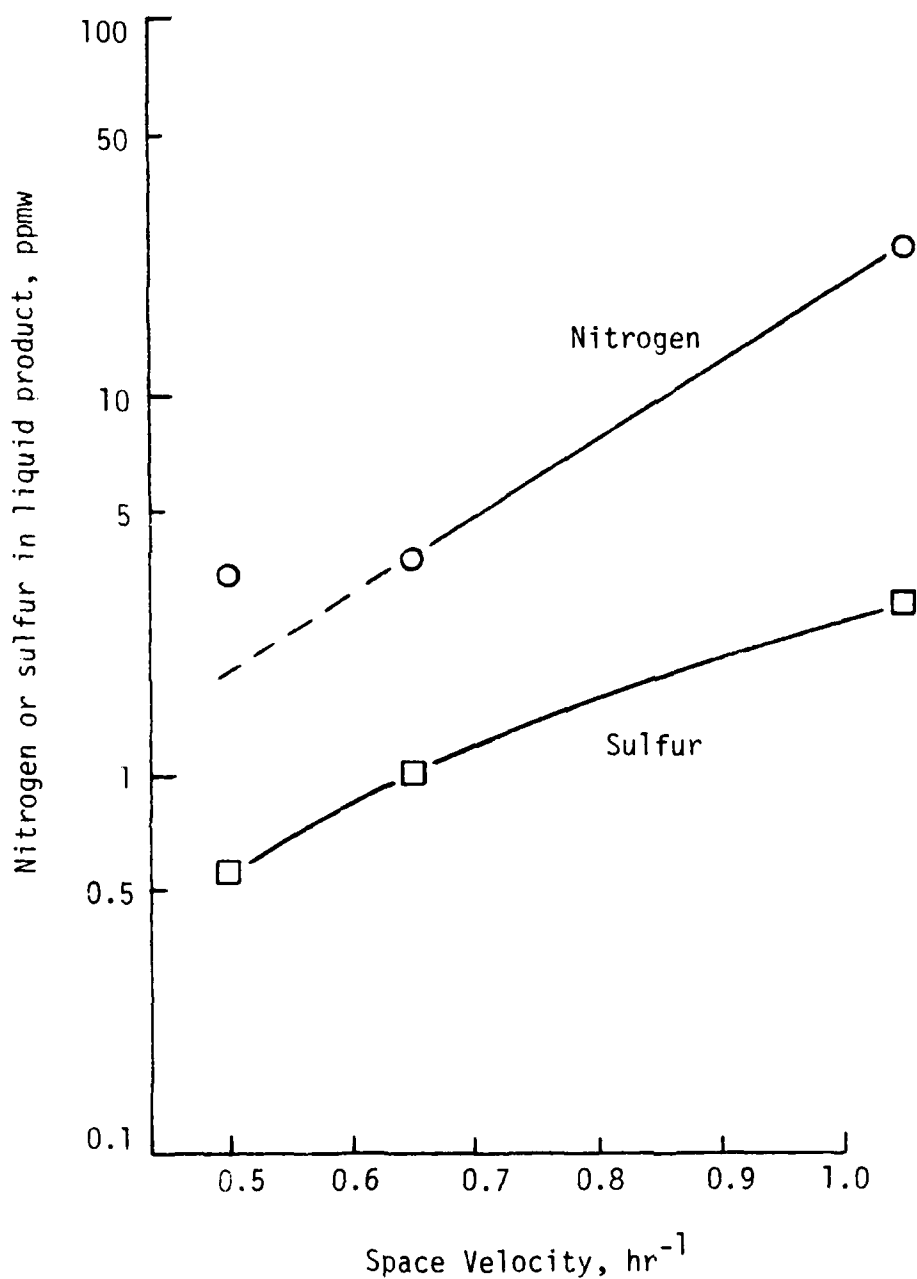


FIGURE 21 HYDROTREATING SUNNYSIDE DISTILLATE;
SPACE VELOCITY EFFECT

Conditions: Ni-Mo on alumina catalyst
750°F average bed temperature
0.5 hr⁻¹ space velocity
feed - hydrovisbroken gas oil
3,380 ppmw nitrogen
2,400 ppmw sulfur

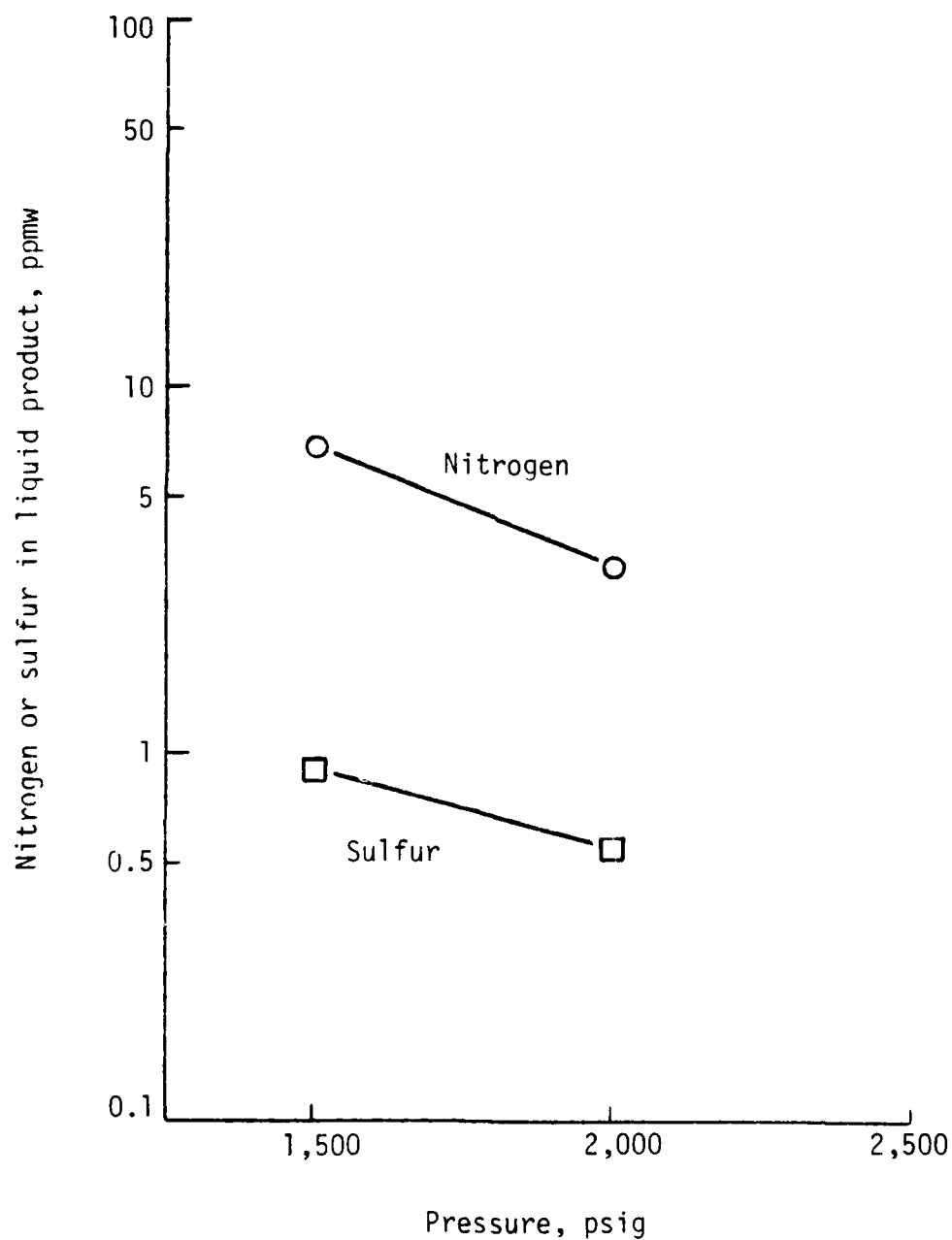


FIGURE 22 HYDROTREATING SUNNYSIDE DISTILLATE;
PRESSURE EFFECT

g. Comparison of feeds

Table 8 summarizes the distillate hydrotreating studies, listing processing conditions and material balance data for the least severe operating condition which resulted in product nitrogen contents in the desired range. Since each of the four feedstocks was processed over a range of severities wide enough to generate both acceptable and unacceptable product quality, the conditions shown in Table 8 are somewhat better reflections of feedstock character than were obtained in the naphtha studies.

Processing requirements appear to be strongly related to feedstock nitrogen content. San Ardo distillate required the most extreme conditions to lower the 8,030 ppmw nitrogen to the 10 ppm range. The other three feeds, with 3,380 to 5,440 ppmw nitrogen, were about comparable and required somewhat milder conditions than the San Ardo.

Hydrogen sulfide yields were highly correlated with feed sulfur and reflect virtually complete removal of the sulfur. C₅+ liquid product yields were in the 101 to 106 volume percent range for all, while only about 1 weight percent of the feeds was reduced to light hydrocarbons. Although the latter suggests hydrocracking was not extensive, the large changes in API gravity, from feed to product, suggest considerable molecular weight reduction has occurred. In fact, simulated distillations of some of the liquid products indicate enough of the charge has been reduced into the turbine fuel distillation range that fractionation of the hydrotreater effluent should be considered before further hydrocracking is performed.

The increase in API gravity, from feed to product, for the Hondo Monterey distillate was 14.0°, compared to 7.8° for Sunnyside, 10.7° for Kensyntar, and 10.9° for the severely processed San Ardo. Thus, extensive sulfur reduction appears to produce additional decreases in product density.

TABLE 8

SUMMARY OF DISTILLATE HYDROTREATING STUDIES

<u>Feed source</u>	<u>Hondo Monterey</u>	<u>San Ardo</u>	<u>Kensyntar</u>	<u>Sunnyside</u>
<u>Feed properties</u>				
Gravity, °API	21.3	17.2	18.9	22.8
Nitrogen, ppmw	5,440	8,030	4,210	3,380
Sulfur, wt.%	3.5	1.5	1.2	0.24
<u>Processing conditions</u>				
Catalyst	Nickel-molybdenum on alumina			
Avg. bed temperature, °F	750	750	750	750
Pressure, psig	2,000	2,500	1,500	2,000
Space velocity, hr ⁻¹	0.75	0.67(1)	0.5	0.7
Hydrogen feed, SCF/bbl	6,000	6,000	6,000	6,000
Hydrogen consumed, SCF/bbl	1,452	698	1,217	415
<u>Results</u>				
Product dist'n, wt.%				
H ₂ S	3.1	1.5	1.0	0.3
C ₁	0.2	0.3	0.3	0.3
C ₂	0.3	0.2	0.3	0.0
C ₃	0.6	0.3	0.5	0.6
C ₄	0.9	0.7	0.5	1.2
C ₅	0.4	0.7	0.6	0.3
C ₆	-	0.2	0.2	0.1
Liquid product	94.4	96.0	96.6	97.2
Product yield, vol.%	103.1	104.1	105.0	99.9
C ₅ + product, vol.%	103.7	105.0	106.2	101.1
<u>Product properties</u>				
Gravity, °API	35.3	28.1	29.6	30.6
Nitrogen, ppmw	2.6	18.7	6.1	3.0
Sulfur, ppmw	4.9	9.8	2.3	0.8

- (1) At 0.5 space velocity, product nitrogen was 5.0 ppmw, but weight balance data were not satisfactory.

h. Preparation of hydrocracking chargestocks

A companion objective of the distillate hydrotreating process studies was preparation of adequate volumes of low nitrogen content liquid to support process scouting studies of the distillate hydrocracking step. As the preceding narrative made clear, many of the runs yielded liquid product with high (i.e. $\gg 10-20$ ppmw) nitrogen content, in the course of defining one or more combinations of acceptable operating conditions. Even when those runs produced satisfactory product, the required space velocity was so low (e.g., from 0.25 to 0.75 hr^{-1}) that the actual volume of product accumulated was much too small to be useful.

This low output argued against employing the same facility to refine the remaining volumes of feed. At least 20 gallons of each distillate, hydrotreated to a nitrogen content of 10 ppmw or less, were needed for the hydrocracking studies. To process each feed at its respective severity level could have required over six months of operating time. Larger fixed bed ARD pilot units would have reduced the time and costs considerably, but were committed to other projects and interrupting the work was not feasible.

An alternative approach utilized the same 10-gallon stirred autoclave that had previously been used in the hydrovisbreaking studies. The equipment was described in Section IV, but the procedure differed somewhat from that used during hydrovisbreaking, and is described below.

One gallon of catalyst was charged to the autoclave, which was then inerted and pressure tested. The catalyst was pre-sulfided using a carbon disulfide in kerosene solution according to the catalyst vendor's instructions. Sulfur content of the kerosene was 100% in excess of the stoichiometric amount calculated for complete conversion of the supported metals to the sulfided form. Following discharge of the sulfiding solution, two low severity runs were made with a coker gas oil feed to condition the catalyst. This step was found necessary to avoid premature deactivation of the catalyst by exposure to an "active" feed at high severity immediately after the pre-sulfiding operation. On completion of

the break-in runs, all four feeds were processed in sequence over the same charge of catalyst, which remained behind as each liquid batch was pressured out of the autoclave via the dip tube arrangement.

A typical run comprised charging, under flowing nitrogen, 5 gallons of unprocessed distillate to the autoclave, which already contained the activated catalyst. After purging and pressure testing, the autoclave was pressured to about 500 to 1,000 psig with hydrogen. With continual high speed stirring, the heating mantle was activated to bring the autoclave contents to the target reaction temperature --generally about 740°F. When necessary, additional hydrogen was admitted to the autoclave to maintain the desired reaction pressure.

Uptake of hydrogen was rapid at first but decreased gradually as the run continued. For safety reasons, direct sampling of the liquid during a run was not practicable, which meant the entire system had to be cooled to below 300°F. Analyses of liquid samples indicated only partial reduction of nitrogen had occurred through the time when hydrogen uptake ceased. However, replacing the remaining gas with fresh hydrogen allowed the hydrodenitrogenation reaction to continue, once the autoclave and contents were reheated to reaction temperature. In fact, multiple cycles of this rather cumbersome procedure were required, to reduce nitrogen content to the desired range:

- charge fresh liquid under nitrogen flow
- nitrogen pressure test
- displace nitrogen with hydrogen by successive pressuring/venting
- hydrogen pressure test at run pressure
- partially vent hydrogen to target pressure
- heat reactor with continued agitation
- maintain desired reaction conditions of temperature, pressure
- admit additional hydrogen to maintain reaction pressure
- continue until rate of pressure drop falls below target value
- cool reactor to below 300°F
- partially vent vapor space through vapor condenser system

- remove and save any condensed (at 100°F and 32°F) liquids collected
- admit fresh hydrogen via successive pressuring, depressuring of reactor (3 X, minimum) with hydrogen
- reheat autoclave to reaction temperature
- repeat the above, excluding first four steps

Using this procedure, an inventory of 15 to 20 gallons of hydrotreated distillate was accumulated for each of the four feed types. The extent of processing, as represented by the number of hydrogenation cycles, varied with the feed quality. Distillate from the hydrovisbroken Sunnyside required only two cycles, while the San Ardo distillate blend required four cycles. Table 9 summarizes results of one batch hydrorefining run for each of the four feeds. As indicated, product nitrogen contents were comfortably within the target 10 ppmw. Product sulfur contents were even lower than the nitrogen levels. All product batches were composited according to feed type and retained for the hydrocracking studies.

Some cracking and/or hydrocracking is inevitable when hydrodenitrogenation of this magnitude is accomplished. Comparative gas chromatographic simulated distillations for one of the Kensyntar runs confirmed this:

ASTM D-2887
Simulated distillation, °F

<u>% Off</u>	<u>Feed</u>	<u>Product</u>
10	572	379
30	682	461
50	764	546
70	842	658
90	922	759

The presence of significant amounts of material already within the turbine fuel boiling range was cause for concern. If allowed to remain when the liquid was hydrocracked, additional molecular weight reduction was likely, shifting product distribution toward light ends. Removal of the light front end by distillation would avoid this distortion but with some loss in schedule, cost and feedstock inventory.

TABLE 9
BATCH HYDROTREATING OF DISTILLATES

Feedstock Source	Cycle No. (2)	Conditions (1)		Time, hrs (3)	Liquid Analysis		Product Fractionation (4)	
		Temp., °F	Press., psig		Nitrogen, ppmw	Sulfur, ppmw	Overhead, Vol. %	Bottoms, Vol. %
Hondo Monterey	Feed	-	-	-	5,440	35,000		
	1	730	2,000	14	-	-		
	2	760	2,250	12	270	-		
	3	730	3,000	4	77	4.2		
Composite (12.7 gal.)	4	740	2,500	9	2.5	nil		
							15.1	84.9
San Ardo	Feed	-	-	-	8,030	15,000		
	1	740	2,700	18	-	-		
	2	740	2,500	13	-	-		
	3	740	2,500	10	39	86.5		
Composite (12.9 gal.)	4	740	2,500	14	1.4	nil		
							15.1	84.9
Kensyntar	Feed	-	-	-	4,210	12,000		
	1	730	2,000	12	300	64		
	2	730	2,000	12	58	26		
	3	730	2,500	14	0.1	0.02		
Composite (10.8 gal.)							15.3	84.7
Sunnyside	Feed	-	-	-	3,380	2,360		
	1	740	2,500	12	-	-		
	2	740	2,500	12	2.7	2.2		
Composite (11.2 gal.)							20.2	79.8

- (1) Five gallons charged to 10-gallon autoclave containing 1 gallon Nickel-molybdenum on alumina catalyst.
(2) Cycle consisted of: react, cool to 300°F, vent vapor space; replace with fresh hydrogen, reheat system
(3) Time at indicated reaction temperature; no further hydrogen uptake apparent.
(4) Distillation yields for composite of several batches; overhead used for blending fuel samples, bottoms for hydrocracking feed.

The composite lots of hydrotreated distillate were batch distilled to remove a portion of the front end already within the JP-4 boiling range. Rather than strip out all of the JP-4 boiling range liquid, still conditions were adjusted in an attempt to approximate the distillation range of the liquids produced in the continuous mode hydrotreating work. Overhead fractions ranged from 15 to 20 volume percent of the hydrotreated distillate charged to the still. Overhead fractions were retained for inclusion in the prototype fuel blends. The bottoms fractions from the stripping operation became the feedstocks for the hydrocracking studies, to be described.

SECTION VI

HYDROCRACKING

1. Introduction

During hydrocracking, distillate boiling range material is refined into high yields of aviation turbine fuel. Hydrocracker feed must be exceptionally clean, to avoid catalyst deactivation. Pretreatment of hydrocracker feed is usually accomplished in a guard-case operation (e.g. in R-1 of a two-reactor train), as was described in the preceding Section V on Hydrotreating.

In the R-2 reactor, hydrocracking reactions reduce the feed molecular weight and distillation properties to more desirable ranges. Should complete conversion of the feed be desired, it is usually advantageous to operate at conditions somewhat less severe than those required for 100% conversion per pass, with separation and recycle of the unconverted portion of the feed. Compared to once-through high conversion, recycle-to-extinction mode of operation yields more beneficial product distribution and prolongs catalyst life. In this study, however, equipment limitations did not permit evaluation of recycle mode hydrocracking. Therefore, once-through type runs covered a relatively wide range of feed conversion level, within which interpolation would permit feedstock comparison at uniform conversion levels.

Study objectives included a brief assessment of process operating conditions. However, because feed inventory was limited, and effective space velocities were expected to be high, only a cursory study of a single process parameter was possible. A second objective was the generation of sufficient quantities of hydrocracked product to permit blending of prototype aviation fuels. Finally, as in all other program elements, any significant feedstock effects were to be identified.

2. Feedstocks

Feedstocks were the four topped fractions from the batch hydrotreated distillates, produced as described in the preceding Section V. Table 10 lists some physical and chemical characteristics of the four feeds. As a result of the extensive processing they had undergone, the distillates have lost many of their distinctive features. Thus, nitrogen and sulfur contents for all four feeds are within the range of about 0.4 to 6 ppmw. Distillation ranges and API gravities were also similar. In one departure from this pattern, aromatics content of the material derived from the Sunnyside bitumen is only about half that of the other three materials. However, further details of the hydrocarbon types contained in the non-aromatic portion of the feed are not provided by the particular analytical method employed.

3. Procedure

The experimental facility was that used for the continuous mode distillate hydrotreating studies. Catalyst charge to the reactor was 100 cc, diluted with inert to provide 33 volume percent active material within the reaction zone.

The hydrocracking catalyst was an experimental composition, consisting of nickel and molybdenum oxides on a crystalline silica-alumina support. It was selected on the basis of the bench scale activity screening tests described in Section III. The catalyst was presulfided before use by the same procedure used to activate the hydrotreating catalyst, described in Section V-2. Start-up and break-in operations over the freshly activated catalyst were with a thoroughly hydrotreated coker gas oil derived from Athabasca bitumen. Product monitoring indicated catalyst activity had stabilized after about 7 days operation, whereupon trials with the test feeds were begun.

Feedstock inventories limited the amount of process variable scouting, since high space velocities, and therefore high liquid feed rates, were anticipated. All runs were on a once-through basis. To

TABLE 10

DISTILLATE HYDROCRACKING FEEDSTOCKS

<u>Source</u>	<u>Hondo Monterey</u>	<u>San Ardo</u>	<u>Kensyntar</u>	<u>Sunnyside</u>
<u>Physical properties</u>				
Gravity, °API	34.1	33.7	32.4	33.8
Sp. gravity, 60/60°F	0.8545	0.8565	0.8635	0.8560
Distillation, °F 0 ____ % (by ASTM D1160)				
IBP	400	394	383	429
5	426	412	414	439
10	441	420	433	458
20	474	439	467	486
30	509	472	502	510
40	542	504	533	535
50	574	538	562	561
60	609	575	594	597
70	652	613	617	636
80	706	669	682	683
90	779	760	742	744
95	832	798	804	789
<u>Chemical analysis by weight</u>				
Nitrogen, total, ppm	5.5	1.4	0.4	0.7
Sulfur, ppm	6.2	4.5	2.3	6.2
Aromatics, wt.% (by D2007)	24.1	25.5	20.3	12.1

achieve the desired wide range of feed conversion, runs were performed at uniform temperature and pressure, but at three different space velocities.

4. Results

Each of the four feedstocks was processed at 610°F and 2,000 psig within a space velocity range of 2 to 5 hr⁻¹. Results were expressed in terms of conversion or disappearance of that material in the feed which boils above 500°F, the nominal upper limit for JP-4 type turbine fuel. As was indicated in Table 10, the fraction boiling above 500°F ranged from about 60 volume percent in the San Ardo feed to about 75 volume percent in the Sunnyside feed.

Figure 23 illustrates the space velocity effect on conversion of the >500°F fraction for each of the four feeds. The consistent trend toward higher conversion levels at successively lower space velocities is as expected. For two feeds, no >500°F fraction remained after processing at the most severe operating condition. This result might be viewed as a conversion exceeding 100%, since the product distillation showed a final boiling point lower than 500°F. While a conversion exceeding 100% has no physical significance, the point is made to emphasize that the 100% conversion points incorporate some ambiguity in their positioning on the chart.

The space velocity-conversion relationships varied modestly with feed origin. Distillate feed prepared from Kensyntar bitumen appeared to be the most difficult to hydrocrack, the distillate from the San Ardo crude somewhat less so, while those prepared from the San Ardo crude and the Sunnyside bitumen were most readily hydrocracked.

Figure 24 illustrates trends in product distribution with estimated conversion of the >500°F fraction in the feed. The trends are directionally similar for all four feeds. Yields of lighter products (e.g. C₃ fraction, C₄ fraction, and the C₅-500°F turbine fuel fraction) increased regularly with the extent of conversion of the >500°F cut. Hydrogen consumption also increased with conversion level, as did the change in ratios of feed to liquid product specific gravities.

Conditions: Ni-Mo on zeolite catalyst
610°F average bed temperature
2,000 psig
feed - hydrotreated distillate;
source as indicated

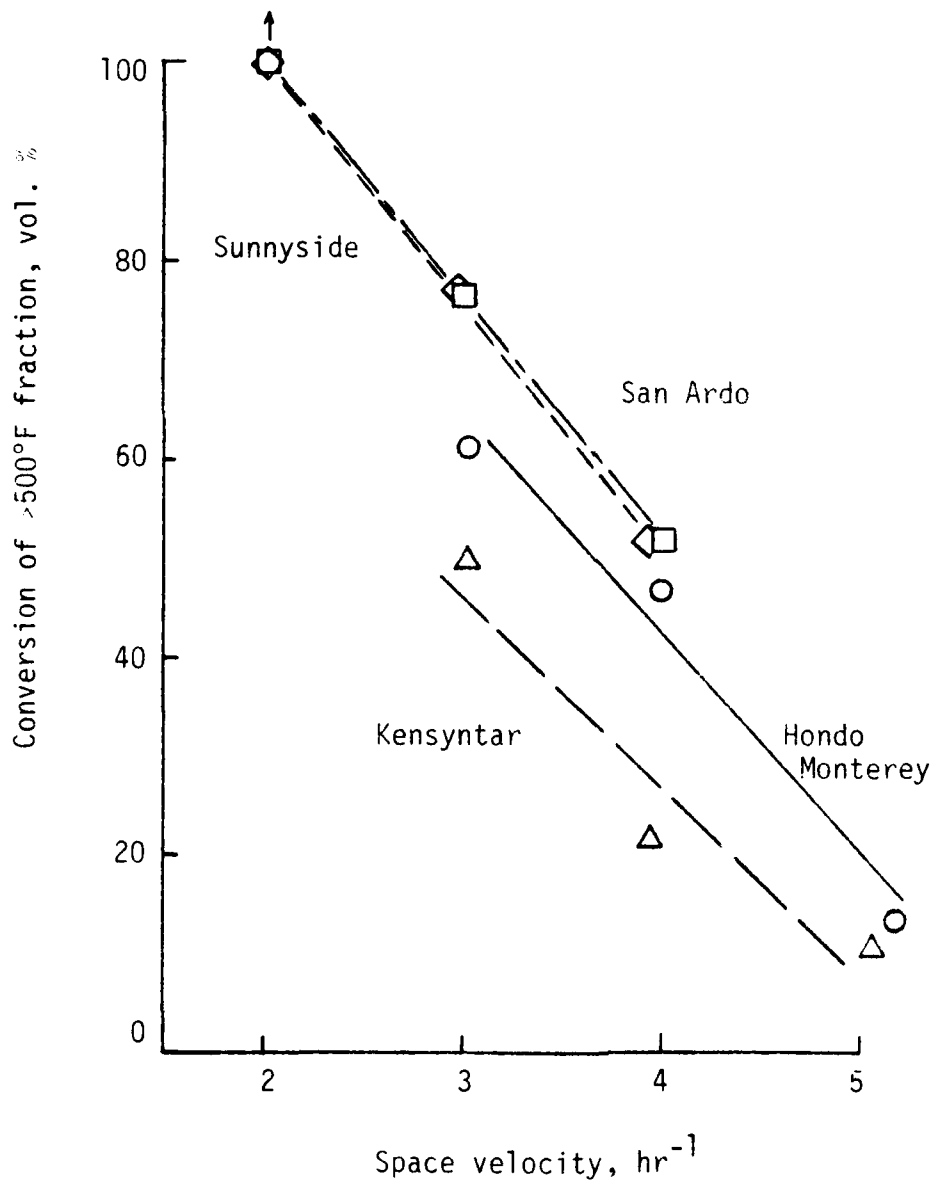
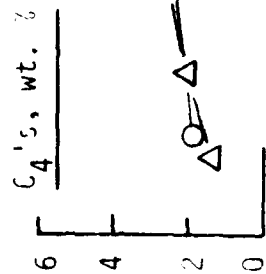


FIGURE 23 DISTILLATE HYDROCRACKING RESULTS

Conditions: 610°F; 2000 psig; Ni-Mo on zeolite catalyst

Feed: ○ Hondo Monterey
□ San Ardo



◇ Kensyntar
△ Sunnyside

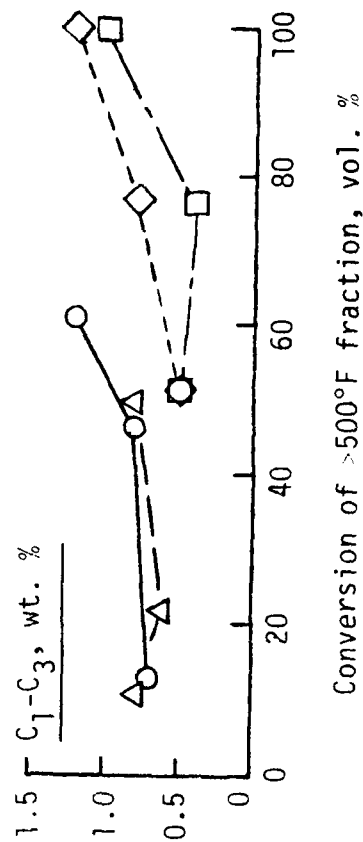
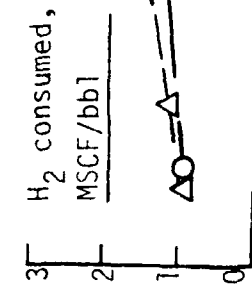
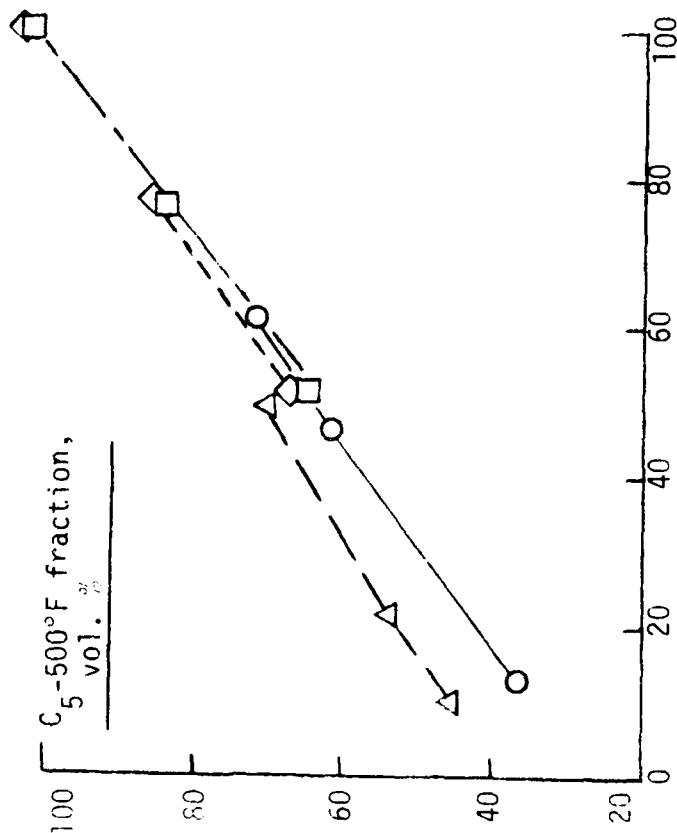
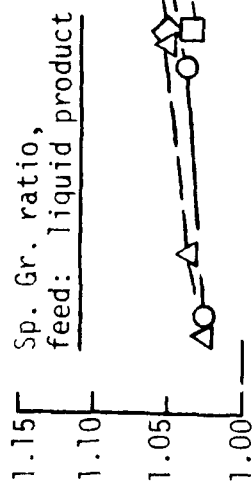


FIGURE 24 HYDROCRACKING PRODUCT DISTRIBUTIONS

AD-A171 565

TURBINE FUELS FROM TAR SANDS BITUMEN AND HEAVY OIL PART 2/2
2 PHASE II LABORA. (U) SUN REFINING AND MARKETING CO
MARCUS HOOK PA APPLIED RESEARCH.. A F TALBOT ET AL.
MAY 86 AFMAL-TR-85-2013-P1-2 F/G 21/4 NL

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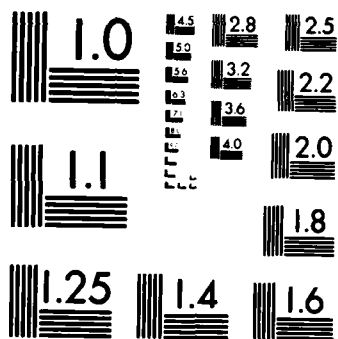
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MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

The trend lines for individual feedstocks in Figure 24 include some irregularities, and several points could be plotted off-scale (at >100% conversion). While these effects make definitive feedstock comparisons somewhat tenuous, it appears all data points could be represented by a fairly narrow band. Some possible exceptions, at comparable conversion levels, include:

- Kensyntar distillate produced slightly more turbine fuel than the other feeds
- San Ardo distillate produced slightly less C₃ and C₄ fractions than the others
- the relative change in liquid density across the reactor was slightly higher for the two bitumen-derived distillates

For all feeds, dry gas (C₁ and C₂'s) yields were nil or nearly so. The C₄ fraction was principally isobutane except for the San Ardo feed, where the C₄ fraction included 20% to 33% normal butane. Product distributions estimated from Figure 24 for all four feeds at 60% conversion are listed in Table 11. They are generally consistent with the preceding discussion. However, these results are only for processing in the R-2 or hydrocracking reactor. As noted earlier, some hydrocracking also occurs in the R-1 operation. To determine the overall yield from the combined operation, the two yield structures should be combined.

TABLE 11
SUMMARY OF DISTILLATE HYDROCRACKING STUDIES

<u>Feed source</u>	<u>Hondo Monterey</u>	<u>San Ardo</u>	<u>Kensyntar</u>	<u>Sunnyside</u>
<u>Feed properties</u>				
Gravity, °API	34.1	33.7	32.4	33.8
Nitrogen, ppmw	5.5	1.4	0.4	0.7
Sulfur, ppmw	6.2	4.5	2.3	6.2
<u>Processing conditions</u> (1)				
Catalyst	Nickel-molybdenum on crystalline silica-alumina			
Avg. bed temperature, °F	←————— 610 —————→			
Pressure, psig	←————— 2000 —————→			
Space velocity, hr ⁻¹	3.2	3.7	2.2	3.7
Hydrogen feed, SCF/bbl	7,600	7,400	7,500	7,100
Hydrogen consumed, SCF/bbl	1,539	1,735	1,767	1,560
<u>Results</u>				
Product dist'n, wt.%				
C ₁	-	-	-	-
C ₂	0.1	-	-	-
C ₃	1.1	0.5	0.9	0.6
C ₄	3.7	2.3	3.5	3.3
C _{5,6}	0.7	0.4	0.6	1.4
Liquid product	94.4	97.3	95.0	94.7
C ₅ +liquid, vol.%	100.2	101.1	101.1	102.0
C ₅ -500°F, vol.%	71.2	71.5	76.8	73.5
Product properties				
Gravity, °API	42.7	40.2	41.6	43.2

(1) Process conditions and product distributions interpolated or extrapolated to 60 volume % conversion of the >500°F fraction in feed.

SECTION VII

FUEL SAMPLES

1. Introduction

Contract performance requirements include preparation of small (i.e. <0.5 liter) samples of aviation turbine fuel made according to the proposed process sequence. This goal was met utilizing the retained liquid products from the various process studies described in Sections IV through VI. The liquids were blended in volumetric proportions approximating the yields obtained in the various process steps, distilled into a number of cuts, and the appropriate distillation cuts then re-blended to obtain the final fuel samples. Limited testing was performed to confirm that the samples represented the types intended. Subjecting the samples to the full battery of specification tests for military grade JP-4 and JP-8 fuels was considered premature, given the exploratory nature of these studies.

2. Component Blending and Fractionation

Retains from the laboratory unit process studies were thoroughly blended prior to fractionation. Three components were used in each blend:

- liquid product from the naphtha hydrotreating studies
- light front end distilled from the batch hydrotreated gas oils
- liquid product from the distillate hydrocracking studies

The components were combined in estimated yield proportions based on the starting heavy crude or bitumen. Although the heavy crudes included a significant amount of straight run material which had bypassed the hydrovisbreaker, the blend proportions for both the two heavy crude feeds and the two bitumen feeds were similar:

Blend components, volume%

<u>Type/source</u>	<u>Hydrotreated Naphtha</u>	<u>Fore-cut from hydrotreated gas oil</u>	<u>Hydrocracked gas oil</u>
Hondo Monterey	48	7	45
San Ardo	45	8	47
Kensyntar	44	8	48
Sunnyside	44	8	48

Approximately 10 gallons of each blend were prepared. Blends were fractionated in a 5-gallon batch still equipped with a stainless steel mesh fractionating column equivalent to 15 theoretical plates. Distillations were performed at a very low reflux ratio (about 1:10) to avoid the overly narrow separation achievable with this equipment. Half of each masterblend was used to prepare distillation cuts for blending a naphtha type (JP-4) turbine fuel sample; the other half, to prepare cuts for blending a kerosene type (JP-8) sample. The distillations were performed at atmospheric pressure through 450°F vapor temperature. Beyond that temperature, the distillations were at 30 mm Hg absolute to avoid cracking or polymerization. Within 24 hours of the distillation, each overhead fraction was treated with an approved butylated phenol type antioxidant at 8 pounds per thousand barrels dosage, to reduce storage stability problems.

Small trial blends, prepared in various combinations of heart cut plus neighboring cuts, determined which fractions should be included in the final blends. For the lower boiling forecuts, fuel front end volatility (RVP for JP-4; flash point for JP-8) controlled blend composition. Fuel freeze point determined which of the fractions boiling higher than the heart cut were included. Both trial blends and final blends were prepared by reconstitution using the same volumetric proportions of heart cut and narrow cuts as were obtained during the fractionation.

3. Fuel Blends

The overhead cut points during the distillations for the two fuel types, regardless of the feedstock source, were:

Distillation Range of Overhead Fractions, °F

Naphtha Type

Initial to 120
120 to 150
150 to 450
450 to 475
475 to 500
500 to 525

Kerosene Type

Initial to 275
275 to 300
300 to 325
325 to 350
350 to 525
525 to 550
550 to 575
575 to 600

The respective heart cuts, underlined in the above listing, were included in each blend. Inclusion or exclusion of the adjacent distillation fractions was determined by testing small trial blends. Tables 12 and 13 list the yields of the cuts made for blending naphtha or kerosene type fuels, respectively. Fractions included in the final fuel sample blends are underscored. Figure 25 illustrates representative distillation curves for the four different masterblends, and indicates the relative position of the heart cuts and adjacent cuts for either the naphtha or kerojet type distillation. An unusual feature of the masterblend prepared from the Sunnyside components is the bulge appearing in the 300° to 450°F temperature range. Similar features appear in the distillation curves of the Sunnyside naphtha before hydrotreating as well as in the liquid products from hydrocracking Sunnyside hydrovisbroken distillate. While it was suspected that the Sunnyside bitumen had not been completely stripped of the kerosene solvent in which it was delivered, it is not known if the presence of residual solvent was the source of the unusual pattern in the final product distillation.

Table 14 lists results of tests performed on the four naphtha type turbine fuel sample blends for comparison with limiting values contained in specification MIL-T-5624L Turbine Fuel, Aviation, Grades JP-4 and JP-5. All four samples had excellent color, with API gravities about in the middle of the allowable range. Vapor pressures were either slightly low or just at the lower limit of the range allowed. Upward adjustment of the Reid vapor

TABLE 12
DISTILLATIONS FOR NAPHTHA TYPE FUEL SAMPLES

<u>Type/Source</u>	<u>Hondo Monterey</u>	<u>San Ardo</u>	<u>Kensyntar</u>	<u>Sunnyside</u>
<u>Boiling range of fraction °F</u>	<u>Fraction, volume percent of still charge⁽¹⁾</u>			
Initial to 120°F	<u>2.1</u>	<u>2.5</u>	<u>2.6</u>	<u>3.3</u>
120 to 150	<u>1.6</u>	<u>2.9</u>	<u>2.3</u>	<u>2.2</u>
150 to 450	<u>58.9</u>	<u>63.3</u>	<u>65.4</u>	<u>54.5</u>
450 to 475	6.0	<u>6.7</u>	<u>2.9</u>	13.0
475 to 500	4.5	5.4	3.5	8.4
500 to 525	3.9	4.0	2.8	4.1
Bottoms	22.9	15.3	20.5	14.6
Turbine fuel yield, vol. % still charge	62.6	75.4	73.2	60.0

(1) Cuts included in final fuel samples are underlined; samples prepared by blending in yield proportions.

TABLE 13
DISTILLATION FOR KEROSENE TYPE FUEL SAMPLES

<u>Type/Source</u>	<u>Hondo Monterey</u>	<u>San Ardo</u>	<u>Kensyntar</u>	<u>Sunnyside</u>
<u>Boiling range of fraction, °F</u>	<u>Fraction, volume percent of still charge(1)</u>			
Initial to 275	20.1	27.5	27.5	21.0
275 to 300	<u>5.9</u>	<u>3.6</u>	<u>5.9</u>	<u>4.8</u>
300 to 325	<u>5.7</u>	<u>5.7</u>	<u>5.2</u>	<u>3.3</u>
325 to 350	<u>6.5</u>	<u>5.6</u>	<u>6.1</u>	<u>4.0</u>
350 to 525	<u>38.3</u>	<u>42.0</u>	<u>34.7</u>	<u>53.2</u>
525 to 550	3.1	<u>3.5</u>	<u>2.7</u>	1.9
550 to 575	2.9	2.3	2.7	1.9
575 to 600	2.8	1.8	2.6	1.5
Bottoms	14.7	8.0	12.6	8.4
Turbine fuel yield, vol. % still charge	56.4	60.4	54.6	65.3

(1) Cuts included in final fuel samples are underlined; samples prepared by blending in yield proportions.

TABLE 14
NAPHTHA TYPE FUEL BLENDS

<u>Feed Source</u>	<u>Hondo Monterey</u>	<u>San Ardo</u>	<u>Kensyn- tar</u>	<u>Sunny- side</u>	<u>MIL-T-5624L limit JP-4 grade</u>
<u>Properties</u>					
Color, Saybolt	30	28	30	28	(1)
Gravity, °API	52.3	51.0	51.6	50.8	45.0-57.0
Reid vapor pressure, lb	2.0	1.7	2.0	1.8	2.0-3.0
Distillation temp., °F(2)					
IPB	206	209	198	208	(1)
10 vol%	255	255	242	257	(1)
20 vol%	280	280	266	280	266 max
50 vol%	335	340	325	350	365 max
90 vol%	394	399	400	420	482 max
FBP	425	429	440	445	-
Freezing point, °F	-72	-76	-76	-62	-72 max
Viscosity, cSt at -20°C	2.06	2.06	1.93	2.28	-
Copper strip corrosion, 2 hrs @ 100°C	1a	1b	1a	1a	1b max
Total acid number, mg KOH/g	0.010	0.012	0.011	0.010	0.015 max
Existent gum, mg/100 ml	1	1	1	1	7.0 max
Thermal stability, change in Δp , mm Hg	0	0	0	0	25 max
deposit code	0	0	0	0	less than 3
Net heat of combustion, BTU/lb	18,488	18,707	18,688	18,668	18,400 min
Sulfur, total wt%	0.0001	0.00006	0.00004	0.0001	0.40 max
Hydrogen content, wt%	14.42	14.34	14.26	14.25	13.6 min
Aromatics, vol%	8.0	3.8	5.4	6.2	25.0 max
Olefins, vol%	0.0	0.7	0.0	0.0	5.0 max

- (1) To be reported - not limited
(2) By ASTM D2887

pressure by addition of light ends (e.g., about 1 volume percent butane) would be effective, but was not considered essential at this stage in the program. The vapor pressure adjustment would also tend to bring the 20 volume percent distilled temperatures closer to the target value.

Three fuels met the freezing point specification of -72°F , maximum. The freeze point of the Sunnyside fuel blend was about 10°F high. It also had the highest 90% point and final boiling point of the four fuels, even though the blend contained no higher boiling fractions than the heart cut. As noted above, the Sunnyside masterblend from which this fuel sample was prepared showed an unusual distillation curve. Further studies would indicate the best way to bring the freeze point within the specification limit. Approaches might include changes in either the product fractionation (narrower heart cut, closer reblending, higher rectification during the distillation) or in the process sequence (different hydrocracking catalyst, addition of a dewaxing step).

All four fuels exhibited acceptable chemical characteristics, with excellent copper strip corrosion, existent gum and total acid numbers. JFTOT thermal stability was excellent. Fuel hydrogen contents and therefore net heats of combustion were satisfactory. Reflecting the high level of hydroprocessing, sulfur contents were one part per million or less and olefin contents were negligible.

Table 15 presents results of tests performed on the four kerosene type turbine fuels, and compares them with the limits contained in MIL-T-83133A, Turbine Fuel, Aviation, Kerosene Type, Grade JP-8. Many of the observations made regarding the naphtha fuels hold also for the kerosene fuels. The two bitumen-derived samples showed a slight loss of color, for causes unknown. Fuel gravities and front end volatilities were comfortably within limits. Two fuels did not meet the freeze point specification --the Hondo by 4°F and the Sunnyside by 10°F . Fuel low-temperature fluidity was satisfactory in all cases. None of the fuels met the total acid number limit. This is somewhat puzzling, since all the naphtha type blends met the same limit with ease, and such a rapid increase in acid number with boiling point is unexpected. Fuel gum content, corrosivity, and thermal stability again signified excellent fuel quality. Fuel hydrogen contents were generally

TABLE 15
KEROSENE TYPE FUEL BLENDS

<u>Feed Source</u>	<u>Hondo Monterey</u>	<u>San Ardo</u>	<u>Kensyn- tar</u>	<u>Sunny- side</u>	<u>MIL-T-83133A limit JP-8 grade</u>
<u>Properties</u>					
Color, Saybolt	29	29	19	20	(1)
Gravity, °API	45.2	41.3	42.7	43.3	37-51
Flash point, °F	115	112	110	123	100 min
Distillation temp., °F(2)					
IPB	308	321	313	316	(1)
10 vol%	332	344	338	349	367 max
20 vol%	350	365	357	376	(1)
50 vol%	394	411	401	419	(1)
90 vol%	463	477	469	459	(1)
FBP	494	508	502	488	626 max
Freezing point, °F	-54	-64	-62	-48	-58 max
Viscosity, cSt at -20°C	4.12	5.24	4.47	5.66	8.0 max
Copper strip corrosion, 2 hrs @ 100°C	1a	1b	1a	1a	1b max
Total acid number, mg KOH/g	0.029	0.020	0.019	0.017	0.015 max
Existent gum, mg/100 ml	1	1	1	1	7.0 max
Thermal stability, change in Δp , mm Hg	1.0	0	0	0	25 max
deposit code	0	0	0	0	less than 3
Net heat of combustion, BTU/lb	18,606	18,531	18,753	18,581	18,400 min
Sulfur, total wt%	0.00009	0.00004	0.00003	0.00003	0.3 max
Hydrogen content, wt%	14.08	13.80	13.84	13.94	13.5 min
Aromatics, vol%	7.1	6.9	8.0	8.0	25.0 max
Olefins, vol%	0.0	0.0	1.4	0.0	5.0 max

(1) To be reported - not limited

(2) By ASTM D2887

lower than for the naphtha type fuels but well above the spec limit, so fuel heat of combustion was not adversely affected.

Approximately 2 liters of each fuel sample (four naphtha type, four kerosene type) were shipped to Air Force Wright Aeronautical Laboratories for further testing and analysis. In addition, the distillation fractions remaining after preparation of the test blends and the eight sample blends were also shipped to AFWAL for further evaluation.

SECTION VIII

PROCESS ANALYSIS

1. Introduction

In Phase I, a number of process schemes for converting bitumen or heavy crude oil into aviation turbine fuel were examined. The case studies compared estimates of plant operating cost, capital investment, overall thermal efficiency, plus product and byproduct distributions. Coupled with projections of fuel manufacturing cost, this information led to the selection of hydrovisbreaking as the most suited upgrading step, from among the four considered. Information supporting the Phase I studies had varied origins (literature citations, in-house experience, vendor quotations, computer modelling) exclusive of experimental work. The objective of this brief program segment was to review the Phase II experimental results to determine if adjustments to the Phase I projections were indicated.

The process analysis activity considered each major process step in the sequence, but did not undertake generation of all new case studies. Comprehensive comparison of the two Phases was not realized, however, owing to:

- four low quality feedstocks were included in each phase, but only one of them was common to both phases
- the Phase I program included preliminary evaluations of four upgrading processes (delayed coking, hydrovisbreaking, asphalt Residual TreatingTM and fixed-bed residual hydrotreating; Phase II looked only at the leading candidate from these four--hydrovisbreaking.
- several Phase I case studies addressed alternate processes or product slates (e.g., fluid catalytic cracking vs. hydrocracking; a mix of transportation fuels vs. turbine fuel); Phase II concentrated on turbine fuel production using the hydrocracking process.

- Phase I projections assumed fully integrated processes, operating to produce optimum results from each. Phase II was of an exploratory nature, and program objectives, equipment capabilities, cost, or schedule considerations sometimes dictated non-representative operations (batch vs. continuous operation, once-through vs. recycle mode; fresh catalyst vs. middle-of-run condition).

2. Process Effects

Phase I case studies included four feedstocks, viz., three tar sand bitumens and one heavy crude oil. Physical and chemical properties of the feeds were obtained from both published and unpublished sources or were estimated. The feeds acquired and analyzed for the Phase II studies were, largely for reasons of availability, not the same as were assumed for Phase I:

<u>Phase I</u>	<u>Phase II</u>
<u>Bitumens</u>	
Santa Rosa, New Mexico	
Kensyntar, Kentucky	Kensyntar, Kentucky
P.R. Spring, Utah	Sunnyside, Utah
<u>Heavy crude oils</u>	
Santa Maria Valley, California	Hondo Monterey, California San Ardo, California

Only the Kensyntar was common to both phases. Other aspects of the Phase II feeds, e.g., the high solids and extreme diluent contents of the Sunnyside bitumen, the very high nitrogen content of the San Ardo crude, ruled out direct comparisons.

The upgrading/refining sequence consisted of three major process segments --hydrovisbreaking, naphtha hydrotreating, and distillate hydrocracking. The latter included an extensive catalytic feed pretreatment section which has been treated as a discrete process step in the Phase II program.

Table 16 summarizes and compares results of the Phase II work and projections used in developing Phase I case studies. For the hydrovisbreaking segment, Phase I assumed continuous processing, whereas batch mode processing in the 10-gallon autoclave was the only feasible way to produce the quantity of hydrovisbroken liquids needed in the Phase II program. In spite of these differences, laboratory results were generally consistent with the earlier projections, as illustrated in the first two columns of Table 16. For nearly comparable conversion levels, product distributions were similar. The small differences in equivalent reaction times and temperatures are in reasonable balance.

The second two columns of Table 16 summarize naphtha hydrotreating and indicate the Phase II results were obtained at substantially milder conditions, viz. at about 100°F lower temperature, at 250 psig lower pressure, and at about two times the space velocity. The space velocity difference will exert the strongest influence on plant design, resulting in a halving of catalyst loading and reactor volume. The differences in the other two parameters were assumed to have minor effects on projected fuel costs.

The effect of doubling the naphtha hydrotreater space velocity on plant capital, for the two refinery capacities used in the Phase I case studies, is summarized in Table 17. Reductions in battery limits installed costs were only 0.023% and 0.072%, for the 7,500 and 50,000 BPSD refineries, respectively. These ratios reflect only the impact of the reduced size naphtha hydrotreating reactors. Inclusion of the effect of the lower initial catalyst fill, and comparing on a total capital basis, i.e., fixed capital plus working capital, shifts the ratios modestly, to 0.024% and 0.076%. Thus, the impact on the Phase I projections of fuel costs would be negligible.

TABLE 18

PROCESS ANALYSIS SUMMARY

Process segment Program element, Phase Mode of operation Feeds	Hydrovisbreaking		Naphtha Hydrotreating		Distillate Hydrotreating		Distillate Hydrocracking	
	I	II	I	II	I	II	I	II
Continuous	Continuous	Batch	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous
3 bitumens	3 bitumens	2 bitumens	4 naphthas	4 naphthas	4 distillates	4 distillates	4 HT'd	4 HT'd
1 hvy crude	2 hvy crudes	2 hvy crudes					distillates	distillates
Feed properties								
Gravity, API	6.2-10.3	8.5-11.9	39.5-46.5	46.8-52.1	20.5-26.1	17.1-22.8	N.D.	32.4-34.1
Sulfur, wt.	0.8-6.0%	0.3-6.2%	0.11-0.9%	0.06-2.4%	0.39-2.29%	0.24-3.5%	N.D.	2-6 ppm
Nitrogen, wt.	0.3-1.0%	0.8-1.4%	400-1800ppm	239-735ppm	0.11-0.44%	0.34-0.80%	N.D.	0.4-6 ppm
% Dist'd @1000°F, vol%	28-52	45-55	NA	NA	NA	NA	NA	NA
Carbon residue, wt%	10.0-17.4	9.5-13.3	NA	NA	NA	NA	NA	NA
Operating conditions								
Temp., °F	825	775-800	720-740	625-675	730	750	720-770	610
Pressure, psig	2,500	2,500	1,500	1,250	1775-2075	1,500-2,500	1,700-2,000	2,000
LHSV, hr	0.6-0.8	-	1.5	1.2-3.0	0.30-0.40	0.50-0.70	1.2(3)	2.2-3.7(4)
Time (nominal), hrs	-	2	-	-	-	-	-	-
Results								
Conversion of feed, %	67-92	70-80	NA	NA	NA	NA	100(3)	60
Hydrogen consumed, wt% feed	1.2-1.4	0.6-1.6	1.5-2.0	0.7-2.1	-	0.7-2.4	3.4-3.9(2)	2.7-3.1(4)
Products								
H ₂ S, wt%	0.5-3.7	<0.1-4.7	N.D.	0-3.3	Not separ-	0.1-3.1	0.4 to 2.4(2)	- (4)
C ₁ -C ₃ , wt%	5.5-7.0	4.2-6.7	N.D.	0.2-0.8	ately est'd;	0.8-1.1	2.9-3.9(2)	0.5-1.2(4)
C ₁ -450/500°F, vol%	27-45	34-51	102-103	100-101	See column	122-127(2)	122-127(2)	75-82(4)
450/500-1000°F, vol%	54-67	41-55	-	-	no. 7	103-108	0	24-30(4)
C ₅ -490/500°F, vol%	-	-	-	97-100	-	-	98-103(2)	71-77(4)

(1) Actual feeds processed were not those produced in column no. 6; see Section V-4 text for details.

(2) Yield estimates for combined R1-1/R-2 operation.

(3) R-2 operating in recycle-to-extinction mode at 60% conversion per pass.

(4) Estimates of conditions and yields for 80% conversion on once-through basis.

TABLE 17
EFFECT OF REDUCED SEVERITY
NAPHTHA HYDROTREATING

Feed type	Bitumen(1)		Heavy crude(2)	
Refinery capacity, bpsd	7,500		50,000	
<u>Phase I costs, \$MM</u>				
Plant capital, battery limits	134.9		457.3	
Off-sites & tankage	123.8		268.5	
Total fixed capital	258.7		725.8	
Working capital	7.1		39.7	
Total capital	265.8		765.5	
<u>Estimate process severity effects</u>				
<u>Naphtha hydrotreater parameters</u>				
Charge rate, bpsd	2,003	2,003	21,213	21,213
Space velocity, hr ⁻¹	1.5	3.0	1.5	3.0
Bed temperature, °F	675	675	675	675
Pressure, psig	1,250	1,250	1,250	1,250
<u>Reactor parameters</u>				
Shell dimensions				
thickness, inches	4	4	4	4
diameter, feet	6	6	9	9
overall length, feet	24	17	59	36
No. beds	1	1	2	2
Gross metal weight, lb.	105,500	81,750	348,680	235,700
<u>Cost parameters</u>				
Reactor cost, \$	85,475	78,000	304,135	225,420
Installed cost, \$	358,995	327,600	1,277,380	946,764
Δ, % battery limits	0.023		0.072	
Catalyst cost, \$	65,000	32,500	507,000	254,800
Sum, \$	423,995	360,100	1,784,380	1,201,564
Differential cost	\$63,895		\$582,816	
% Total capital	0.024		0.076	

- (1) Projections from case study X-2 of Phase I
(2) Projections from case study X-4 of Phase I

The third pair of columns of Table 16 summarizes conditions for the operation of R-1 of the hydrocracker complex and includes the Phase II yield pattern, for the runs made in the laboratory unit. Given the range of feed qualities, the Phase I projections of processing conditions were reasonable. R-1 stage yields could not be compared, however, because they were lumped with the R-2 operation in the Phase I projections.

The final two columns of Table 16 summarize R-2 operations. Phase II shows both a temperature and space velocity advantage. The temperature advantage results from the use of the more active zeolite-based catalyst described in Section III. It would decrease plant operating costs, but the effect was considered not large enough to estimate. The space velocity advantage results from listing Phase II conditions and yield data for 60 volume percent conversion of the feed on a once-through basis --the only region common to all four feeds processed in Phase II-- whereas Phase I assumed 100% conversion in a recycle operation. Extrapolation of the Phase II data for comparison with Phase I's R-2 projections is not advised. Directionally, however, the effect would be to narrow the spreads between the two sets of results.

Even with such an adjustment to the Phase II R-2 results, and after combining the R-1 and R-2 yields, it is clear there would be a large difference between the C₄ yields observed in Phase II and those projected in Phase I. The unusual C₄ yield projections obtained in Phase I from the computer model hydrocracker simulation have been noted (Reference 1). They are believed the result of applying the model to feeds very unlike those for which the model was constructed. Actual C₄ yields are expected to fall somewhere within the indicated range, but the extent of any correction is so uncertain that none was made. Phase III work should clarify this point, at least for the one feed.

The completed process analysis study thus revealed no significant discrepancies between the Phase I case study projections and the Phase II bench scale work.

SECTION IX

CONCLUSIONS

1. A process for the conversion of bitumen or heavy crude oils into high quality military type aviation turbine fuels has been demonstrated in laboratory or bench scale equipment.
2. The process sequence consisted of an upgrading step, in which the bitumen or atmospheric crude residue was first converted to lower boiling liquid fractions in a high temperature, high hydrogen pressure environment. We have used the term hydrovisbreaking to identify this step. Distillable liquids from the first step were then combined with any liquids distilled from the raw feed and catalytically hydrotreated to reduce heteroatoms and other contaminants to low levels. Finally, hydrotreated liquids which boiled above the desired temperature range were catalytically hydrocracked to increase further the yields of aviation turbine fuel.
3. All of the principal process steps were carried out with each of four low quality feedstocks, albeit not in a fully integrated fashion. In some cases, batch processing was more expedient than continuous mode operation to meet the various project goals. Based on the four feeds tested, the process appears capable of handling a wide range of heavy feedstocks. Modest adjustments in processing severity were required in several of the process steps, reflecting either the refractoriness of the charge or its nitrogen content.
4. Prototype aviation turbine fuels were blended and distilled from reactor products representing each of the four feedstocks. Both naphtha and kerosene type fuels were prepared and tested. Comparison with specification limits for JP-4 and JP-8 fuels was generally

excellent. Freeze points of both the naphtha- and the kerosene-type fuels from one feedstock --Sunnyside (Utah) bitumen-- were out of spec by 10°F. While the matter was not pursued in these studies, it is not presently considered a major problem with either the process sequence or with the particular feedstock.

5. To the extent allowed, these Phase II results were compared with the Phase I case studies on which the process recommendation was based. No significant adjustments to the Phase I projections appeared necessary. Some uncertainty in the overall yield of butane remains, however, even after the Phase II experimental work.

SECTION X

RECOMMENDATIONS

1. These Phase II studies, while preliminary, have shown that the recommended process sequence is capable of producing high quality aviation turbine fuels, suitable for military use, from extremely low quality feedstocks. Further, these laboratory scale experiments were found generally consistent with the projections on which the Phase I case studies were based. It is therefore recommended that the Phase III or pilot plant scale segment of this program continue, with the demonstration of the process on a larger volume scale using continuous mode facilities. This will permit production of larger volume samples for more extensive testing, and generation of more representative operating data to support a detailed process design and refined fuel cost estimates.
2. At the conclusion of these studies, a technical operating report was submitted to the Air Force project officer, in which detailed plans for a Phase III program were presented for approval. Since the process appears to be relatively feedstock insensitive, the plan was based on use of only one feed. Capability to manufacture either JP-4 or JP-8 in high yields continues to be of interest, so the overall refinery configuration included in the plan was shaped accordingly.

REFERENCES

1. A. F. Talbot, V. Elanchenny, L. H. Finkel, A. Macris, and J. P. Schwedock, "Turbine Fuels from Tar Sands Bitumen and Heavy Oil; Phase I, Preliminary Process Analysis" AFWAL-TR-85-2013; Report prepared for the Department of Defense U.S. Air Force by Applied Research and Development Department, Sun Refining and Marketing Company under Contract No. F33615-83-C-2352; 1985.
2. L. C. Marchant and R. E. Terry, "U.S. Tar Sand Oil Recovery Projects", Symposium papers Synthetic Fuels from Oil Shale and Tar Sands (Louisville, Kentucky, 17-19 May, 1983); sponsored by Institute of Gas Technology, Chicago, Illinois.

Time	Lat	Long	Alt	Speed	Direction	Remarks
00:00	37.0	122.0	1000.0	10.0	000	Clear
00:05	37.1	122.1	1000.0	10.0	000	Clear
00:10	37.2	122.2	1000.0	10.0	000	Clear
00:15	37.3	122.3	1000.0	10.0	000	Clear
00:20	37.4	122.4	1000.0	10.0	000	Clear
00:25	37.5	122.5	1000.0	10.0	000	Clear
00:30	37.6	122.6	1000.0	10.0	000	Clear
00:35	37.7	122.7	1000.0	10.0	000	Clear
00:40	37.8	122.8	1000.0	10.0	000	Clear
00:45	37.9	122.9	1000.0	10.0	000	Clear
00:50	38.0	123.0	1000.0	10.0	000	Clear
00:55	38.1	123.1	1000.0	10.0	000	Clear
01:00	38.2	123.2	1000.0	10.0	000	Clear
01:05	38.3	123.3	1000.0	10.0	000	Clear
01:10	38.4	123.4	1000.0	10.0	000	Clear
01:15	38.5	123.5	1000.0	10.0	000	Clear
01:20	38.6	123.6	1000.0	10.0	000	Clear
01:25	38.7	123.7	1000.0	10.0	000	Clear
01:30	38.8	123.8	1000.0	10.0	000	Clear
01:35	38.9	123.9	1000.0	10.0	000	Clear
01:40	39.0	124.0	1000.0	10.0	000	Clear
01:45	39.1	124.1	1000.0	10.0	000	Clear
01:50	39.2	124.2	1000.0	10.0	000	Clear
01:55	39.3	124.3	1000.0	10.0	000	Clear
02:00	39.4	124.4	1000.0	10.0	000	Clear
02:05	39.5	124.5	1000.0	10.0	000	Clear
02:10	39.6	124.6	1000.0	10.0	000	Clear
02:15	39.7	124.7	1000.0	10.0	000	Clear
02:20	39.8	124.8	1000.0	10.0	000	Clear
02:25	39.9	124.9	1000.0	10.0	000	Clear
02:30	40.0	125.0	1000.0	10.0	000	Clear
02:35	40.1	125.1	1000.0	10.0	000	Clear
02:40	40.2	125.2	1000.0	10.0	000	Clear
02:45	40.3	125.3	1000.0	10.0	000	Clear
02:50	40.4	125.4	1000.0	10.0	000	Clear
02:55	40.5	125.5	1000.0	10.0	000	Clear
03:00	40.6	125.6	1000.0	10.0	000	Clear
03:05	40.7	125.7	1000.0	10.0	000	Clear
03:10	40.8	125.8	1000.0	10.0	000	Clear
03:15	40.9	125.9	1000.0	10.0	000	Clear
03:20	41.0	126.0	1000.0	10.0	000	Clear
03:25	41.1	126.1	1000.0	10.0	000	Clear
03:30	41.2	126.2	1000.0	10.0	000	Clear
03:35	41.3	126.3	1000.0	10.0	000	Clear
03:40	41.4	126.4	1000.0	10.0	000	Clear
03:45	41.5	126.5	1000.0	10.0	000	Clear
03:50	41.6	126.6	1000.0	10.0	000	Clear
03:55	41.7	126.7	1000.0	10.0	000	Clear
04:00	41.8	126.8	1000.0	10.0	000	Clear
04:05	41.9	126.9	1000.0	10.0	000	Clear
04:10	42.0	127.0	1000.0	10.0	000	Clear
04:15	42.1	127.1	1000.0	10.0	000	Clear
04:20	42.2					

TABLE A-1
PROPERTIES OF HONDO MONTEREY FRACTIONS

<u>Fraction</u>	Initial to 120°F	120 to 490°F	490 to 550°F	550 to 650°F	>650°F
Yield, vol. % still charge	1.7	21.2	4.3	8.1	64.7
<u>Physical properties</u>					
Gravity, °API	99.5	49.0	31.9	29.3	8.3
Sp. grav. @ 60/60°F	0.6126	0.7839	0.8660	0.8800	1.0122
Flash point, °F	--	40	224	--	--
Pour point, °F	--	--	--	11	105
Viscosity, cSt @					
100°F	--	--	--	5.37	--
160°F	--	--	--	--	3,128
210°F	--	--	--	1.69	473
Carbon residue, wt. %	--	--	--	0.35	12.9
Ash, wt. %	--	--	--	<0.01	0.11
<u>Chemical characteristics</u>					
Carbon, wt. %	--	84.74	83.06	83.02	81.6
Hydrogen, wt. %	--	13.87	12.46	12.37	10.42
Oxygen, wt. %	--	0.30	0.34	0.49	0.62
Nitrogen, wt. %	--	0.09	0.10	0.16	0.88
Sulfur, wt. %	--	1.24	3.3	3.6	6.25
Basic nitrogen, wt. %	--	0.003	0.043	0.105	0.331
Hydrocarbon type, wt. %					
Asphaltenes	--	--	--	--	28.0
Saturates	--	--	--	--	14.3
Aromatics	--	14.2	44.3	47.1	28.0
Resins	--	--	--	--	29.7
Metals, ppm w					
Nickel	--	--	--	0.05	12.5
Vanadium	--	--	--	0.06	29.0
Iron	--	--	--	0.38	4.4
Copper	--	--	--	0.04	0.3

TABLE A-2
PROPERTIES OF SAN ARDO FRACTIONS

<u>Fraction</u>	Initial to 490°F	490 to 550°F	550 to 650°F	>650°F
Yield, vol. % still charge	9.7	5.4	9.5	75.4
<u>Physical properties</u>				
Gravity, °API	34.7	27.0	23.7	8.5
Sp. grav. @ 60/60°F	0.8514	0.8927	0.9117	1.0107
Flash point, °F	115	235	--	--
Pour point, °F	--	--	-56	>120
Viscosity, cSt@				
100°F	--	--	8.47	--
160°F	--	--	--	7,570
210°F	--	--	2.02	788
Carbon residue, wt.%	--	--	0.28	11.6
Ash, wt.%	--	--	0.01	0.053
<u>Chemical characteristics</u>				
Carbon, wt.%	84.30	84.42	83.70	83.84
Hydrogen, wt.%	12.72	11.95	11.63	10.14
Oxygen, wt.%	0.28	0.28	1.02	1.73
Nitrogen, wt.%	0.018	0.047	0.096	0.76
Sulfur, wt.%	0.71	1.10	1.29	2.04
Basic nitrogen, wt.%	0.005	0.027	0.068	0.316
Hydrogen type, wt.%				
Asphaltenes	--	--	--	21.7
Saturates	--	--	--	16.8
Aromatics	11.7	47.3	39.4	24.9
Resins	--	--	--	36.6
Meals, ppm w				
Nickel	--	--	0.07	4.4
Vanadium	--	--	0.02	6.5
Iron	--	--	0.75	18
Copper	--	--	0.03	0.05

TABLE A-3
PROPERTIES OF KENSYNTAR FRACTIONS

<u>Fraction</u>	Initial to 550°F	550 to 950°F	>950°F
Yield, vol.% still charge	0.5	49.7	49.8
<u>Physical properties</u>			
Gravity, °API	28.2	20.8	too heavy
Sp. grav. @ 60/60°F	0.8661	0.9291	--
Flash point, °F	185	--	--
Pour point, °F	--	-30	>120
Viscosity, cSt @			
100°F	--	36.2	--
160°F	--	--	--
210°F	--	4.68	too heavy
275°F	--	--	21,916
Carbon residue, wt.%	--	11.3	22.5
Ash, wt.%	--	0.02	2.28
<u>Chemical characteristics</u>			
Carbon, wt.%	85.82	86.93	85.72
Hydrogen, wt.%	13.08	11.96	9.58
Oxygen, wt.%	0.69	0.69	1.39
Nitrogen, wt.%	0.0036	0.16	0.89
Sulfur, wt.%	0.36	1.16	1.89
Basic nitrogen, wt.%	0.0037	0.05	0.43
Hydrocarbon type, wt.%			
Asphaltenes	--	--	60.5
Saturates	--	--	9.5
Aromatics	32.7	51.2	6.7
Resins	--	--	23.7
Metals, ppm w			
Nickel	--	0.06	60
Vanadium	--	0.08	128
Iron	--	0.50	740
Copper	--	0.04	10

TABLE A-4
PROPERTIES OF SUNNYSIDE FRACTIONS

<u>Fraction</u>	Initial to 490°F	490 to 550°F	550 to 650°F	>650°F
Yield, vol.% still charge	14.6	6.9	2.4	76.1
<u>Physical properties</u>				
Gravity, °API	41.7	34.3	24.4	5.1
Sp. grav. @ 60/60°F	0.8184	0.8534	0.9018	1.0359
Flash point, °F	200	360	---	---
Pour point, °F	--	--	--	>120
Viscosity, cSt @				
100°F	--	--	i	t
160°F	--	--	n	o
210°F	--	--	s	o
Carbon residue, wt.%	--	--	f	h
Ash, wt.%	--	--	i	e
<u>Chemical characteristics</u>				
Carbon, wt.%	86.84	86.43	e	y
Hydrogen, wt.%	13.54	12.71	n	
Oxygen, wt.%	0.26	0.26	t	
Nitrogen, wt.%	0.019	0.019		
Sulfur, wt.%	0.07	0.15	v	
Basic nitrogen, wt.%	0.003	0.008	o	
Hydrocarbon type, wt.%			l	
Asphaltenes	--	--	u	
Saturates	--	--	m	
Aromatics	12.7	31.5	e	
Resins	--	--		
Metals, ppm w				
Nickel	--	--		
Vanadium	--	--		
Iron	--	--		
Copper	--	--		

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